Unit

1

SOME BASIC CONCEPTS OF CHEMISTRY

I. Multiple Choice Questions (Type-I)

1. Two students performed the same experiment separately and each one of them recorded two readings of mass which are given below. Correct reading of mass is 3.0 g. On the basis of given data, mark the correct option out of the following statements.

Student	Readings	
	(i)	(ii)
A	3.01	2.99
B	3.05	2.95

(i) Results of both the students are neither accurate nor precise.

(ii) Results of student A are both precise and accurate.

(iii) Results of student B are neither precise nor accurate.

(iv) Results of student B are both precise and accurate.

2. A measured temperature on Fahrenheit scale is 200 °F. What will this reading be on Celsius scale?

(i) 40 °C

(ii) 94 °C

(iii) 93.3 °C

(iv) 30 °C

3. What will be the molarity of a solution, which contains 5.85 g of NaCl(s) per 500 mL?

(i) 4 mol L^{-1}

(ii) 20 mol L^{-1}

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(iii) 0.2 mol L^{-1}

(iv) 2 mol L^{-1}

4. If 500 mL of a 5M solution is diluted to 1500 mL, what will be the molarity of the solution obtained?

(i) 1.5 M

(ii) 1.66 M

(iii) 0.017 M

(iv) 1.59 M

5. The number of atoms present in one mole of an element is equal to Avogadro number. Which of the following element contains the greatest number of atoms?

(i) 4g He

(ii) 46g Na

(iii) 0.40g Ca

(iv) 12g He

6. If the concentration of glucose ($C_6H_{12}O_6$) in blood is 0.9 g L^{-1}, what will be the molarity of glucose in blood?

(i) 5 M

(ii) 50 M

(iii) 0.005 M

(iv) 0.5 M

7. What will be the molality of the solution containing 18.25 g of HCl gas in 500 g of water?

(i) 0.1 m

(ii) 1 M

(iii) 0.5 m

(iv) 1 m

8. One mole of any substance contains 6.022×10^{23} atoms/molecules. Number of molecules of H_2SO_4 present in 100 mL of 0.02M H_2SO_4 solution is _____.

(i) 12.044×10^{20} molecules

(ii) 6.022×10^{23} molecules

(iii) 1×10^{23} molecules

(iv) 12.044×10^{23} molecules

9. What is the mass percent of carbon in carbon dioxide?

(i) 0.034%

(ii) 27.27%

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(iii) 3.4%

(iv) 28.7%

10. The empirical formula and molecular mass of a compound are CH_2O and 180 g respectively. What will be the molecular formula of the compound?

(i) $C_9H_{18}O_9$

(ii) CH_2O

(iii) $C_6H_{12}O_6$

(iv) $C_2H_4O_2$

11. If the density of a solution is 3.12 g mL^{-1}, the mass of 1.5 mL solution in significant figures is _____.

(i) 4.7g

(ii) 4680×10^{-3}g

(iii) 4.680g

(iv) 46.80g

12. Which of the following statements about a compound is incorrect?

(i) A molecule of a compound has atoms of different elements.

(ii) A compound cannot be separated into its constituent elements by physical methods of separation.

(iii) A compound retains the physical properties of its constituent elements.

(iv) The ratio of atoms of different elements in a compound is fixed.

13. Which of the following statements is correct about the reaction given below:

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(g)$$

(i) Total mass of iron and oxygen in reactants = total mass of iron and oxygen in product therefore it follows law of conservation of mass.

(ii) Total mass of reactants = total mass of product; therefore, law of multiple proportions is followed.

(iii) Amount of Fe_2O_3 can be increased by taking any one of the reactants (iron or oxygen) in excess.

(iv) Amount of Fe_2O_3 produced will decrease if the amount of any one of the reactants (iron or oxygen) is taken in excess.

14. Which of the following reactions is not correct according to the law of conservation of mass.

(i) $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$

(ii) $C_3H_8(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$

(iii) $P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$

(iv) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O\ (g)$

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15. Which of the following statements indicates that law of multiple proportion is being followed.

(i) Sample of carbon dioxide taken from any source will always have carbon and oxygen in the ratio 1:2.

(ii) Carbon forms two oxides namely CO_2 and CO, where masses of oxygen which combine with fixed mass of carbon are in the simple ratio 2:1.

(iii) When magnesium burns in oxygen, the amount of magnesium taken for the reaction is equal to the amount of magnesium in magnesium oxide formed.

(iv) At constant temperature and pressure 200 mL of hydrogen will combine with 100 mL oxygen to produce 200 mL of water vapour.

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

16. One mole of oxygen gas at STP is equal to _____.

(i) 6.022×10^{23} molecules of oxygen

(ii) 6.022×10^{23} atoms of oxygen

(iii) 16 g of oxygen

(iv) 32 g of oxygen

17. Sulphuric acid reacts with sodium hydroxide as follows :

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

When 1L of 0.1M sulphuric acid solution is allowed to react with 1L of 0.1M sodium hydroxide solution, the amount of sodium sulphate formed and its molarity in the solution obtained is

(i) 0.1 mol L^{-1}

(ii) 7.10 g

(iii) 0.025 mol L^{-1}

(iv) 3.55 g

18. Which of the following pairs have the same number of atoms?

(i) 16 g of O_2(g) and 4 g of H_2(g)

(ii) 16 g of O_2 and 44 g of CO_2

(iii) 28 g of N_2 and 32 g of O_2

(iv) 12 g of C(s) and 23 g of Na(s)

19. Which of the following solutions have the same concentration?

(i) 20 g of NaOH in 200 mL of solution

(ii) 0.5 mol of KCl in 200 mL of solution

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(iii) 40 g of NaOH in 100 mL of solution

(iv) 20 g of KOH in 200 mL of solution

20. 16 g of oxygen has same number of molecules as in

(i) 16 g of CO

(ii) 28 g of N_2

(iii) 14 g of N_2

(iv) 1.0 g of H_2

21. Which of the following terms are unitless?

(i) Molality

(ii) Molarity

(iii) Mole fraction

(iv) Mass percent

22. One of the statements of Dalton's atomic theory is given below:

"Compounds are formed when atoms of different elements combine in a fixed ratio"

Which of the following laws is **not** related to this statement?

(i) Law of conservation of mass

(ii) Law of definite proportions

(iii) Law of multiple proportions

(iv) Avogadro law

III. Short Answer Type

23. What will be the mass of one atom of C-12 in grams?

24. How many significant figures should be present in the answer of the following calculations?

$$\frac{2.5 \times 1.25 \times 3.5}{2.01}$$

25. What is the symbol for SI unit of mole? How is the mole defined?

26. What is the difference between molality and molarity?

27. Calculate the mass percent of calcium, phosphorus and oxygen in calcium phosphate $Ca_3(PO_4)_2$.

28. 45.4 L of dinitrogen reacted with 22.7 L of dioxygen and 45.4 L of nitrous oxide was formed. The reaction is given below:

$$2N_2(g) + O_2(g) \longrightarrow 2N_2O(g)$$

Which law is being obeyed in this experiment? Write the statement of the law?

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29. If two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in whole number ratio.

(a) Is this statement true?

(b) If yes, according to which law?

(c) Give one example related to this law.

30. Calculate the average atomic mass of hydrogen using the following data :

Isotope	% Natural abundance	Molar mass
^{1}H	99.985	1
^{2}H	0.015	2

31. Hydrogen gas is prepared in the laboratory by reacting dilute HCl with granulated zinc. Following reaction takes place.

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

Calculate the volume of hydrogen gas liberated at STP when 32.65 g of zinc reacts with HCl. 1 mol of a gas occupies 22.7 L volume at STP; atomic mass of Zn = 65.3 u.

32. The density of 3 molal solution of NaOH is 1.110 g mL^{-1}. Calculate the molarity of the solution.

33. Volume of a solution changes with change in temperature, then, will the molality of the solution be affected by temperature? Give reason for your answer.

34. If 4 g of NaOH dissolves in 36 g of H_2O, calculate the mole fraction of each component in the solution. Also, determine the molarity of solution (specific gravity of solution is 1g mL^{-1}).

35. The reactant which is entirely consumed in reaction is known as limiting reagent. In the reaction $2A + 4B \rightarrow 3C + 4D$, when 5 moles of A react with 6 moles of B, then

(i) which is the limiting reagent?

(ii) calculate the amount of C formed?

IV. Matching Type

36. Match the following:

(i)	88 g of CO_2	(a)	0.25 mol
(ii)	6.022×10^{23} molecules of H_2O	(b)	2 mol
(iii)	5.6 litres of O_2 at STP	(c)	1 mol
(iv)	96 g of O_2	(d)	6.022×10^{23} molecules
(v)	1 mol of any gas	(e)	3 mol

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37. Match the following physical quantities with units

	Physical quantity		**Unit**
(i)	Molarity	(a)	$g\ mL^{-1}$
(ii)	Mole fraction	(b)	mol
(iii)	Mole	(c)	Pascal
(iv)	Molality	(d)	Unitless
(v)	Pressure	(e)	$mol\ L^{-1}$
(vi)	Luminous intensity	(f)	Candela
(vii)	Density	(g)	$mol\ kg^{-1}$
(viii)	Mass	(h)	Nm^{-1}
		(i)	kg

V. Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

38. ***Assertion (A) :*** The empirical mass of ethene is half of its molecular mass.

Reason (R) : The empirical formula represents the simplest whole number ratio of various atoms present in a compound.

(i) Both A and R are true and R is the correct explanation of A.

(ii) A is true but R is false.

(iii) A is false but R is true.

(iv) Both A and R are false.

39. ***Assertion (A) :*** One atomic mass unit is defined as one twelfth of the mass of one carbon-12 atom.

Reason (R) : Carbon-12 isotope is the most abundant isotope of carbon and has been chosen as standard.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

40. ***Assertion (A) :*** Significant figures for 0.200 is 3 where as for 200 it is 1.

Reason (R) : Zero at the end or right of a number are significant provided they are not on the right side of the decimal point.

(i) Both A and R are true and R is correct explanation of A.

(ii) Both A and R are true but R is not a correct explanation of A.

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(iii) A is true but R is false.

(iv) Both A and R are false.

41. ***Assertion (A) :*** Combustion of 16 g of methane gives 18 g of water.

Reason (R) : In the combustion of methane, water is one of the products.

(i) Both A and R are true but R is not the correct explanation of A.

(ii) A is true but R is false.

(iii) A is false but R is true.

(iv) Both A and R are false.

VI. Long Answer Type

42. A vessel contains 1.6 g of dioxygen at STP (273.15K, 1 atm pressure). The gas is now transferred to another vessel at constant temperature, where pressure becomes half of the original pressure. Calculate

(i) volume of the new vessel.

(ii) number of molecules of dioxygen.

43. Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction given below:

$$CaCO_3\,(s) + 2HCl\,(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

What mass of $CaCl_2$ will be formed when 250 mL of 0.76 M HCl reacts with 1000 g of $CaCO_3$? Name the limiting reagent. Calculate the number of moles of $CaCl_2$ formed in the reaction.

44. Define the law of multiple proportions. Explain it with two examples. How does this law point to the existance of atoms?

45. A box contains some identical red coloured balls, labelled as A, each weighing 2 grams. Another box contains identical blue coloured balls, labelled as B, each weighing 5 grams. Consider the combinations AB, AB_2, A_2B and A_2B_3 and show that law of multiple proportions is applicable.

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ANSWERS

I. Multiple Choice Questions (Type-I)

1. (ii) 2. (iii) 3. (iii) 4. (ii) 5. (iv) 6. (iii)

7. (iv) 8. (i) 9. (ii) 10. (iii) 11. (i) 12. (iii)

13. (i) 14. (ii) 15. (ii)

II. Multiple Choice Questions (Type-II)

16. (i), (iv) 17. (ii), (iii) 18. (iii), (iv)

19. (i), (ii) 20. (iii), (iv) 21. (iii), (iv)

22. (i), (iv)

III. Short Answer Type

23. 1.992648×10^{-23} g $\approx 1.99 \times 10^{-23}$ g

24. 2

25. Symbol for SI Unit of mole is mol.

One mole is defined as the amount of a substance that contains as many particles or entities as there are atoms in exactly 12 g (0.012 kg) of the ^{12}C isotope.

26. Molality is the number of moles of solute present in one kilogram of solvent but molarity is the number of moles of solute dissolved in one litre of solution.

Molality is independent of temperature whereas molarity depends on temperature.

27. Mass percent of calcium $= \frac{3 \times (\text{atomic mass of calcium})}{\text{molecular mass of } Ca_3(PO_4)_2} \times 100$

$= \frac{120\ u}{310\ u} \times 100 = 38.71\%$

Mass percent of phosphorus $= \frac{2 \times (\text{atomic mass of phosphorus})}{\text{molecular mass of } Ca_3(PO_4)_2} \times 100$

$= \frac{2 \times 31\ u}{310\ u} \times 100 = 20\%$

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$$\text{Mass percent of oxygen} = \frac{8 \times (\text{Atomic mass of oxygen})}{\text{molecular mass of } Ca_3(PO_4)_2} \times 100$$

$$= \frac{8 \times 16\ u}{310\ u} \times 100 = 41.29\%$$

28. According to Gay Lussac's law of gaseous volumes, gases combine or are produced in a chemical reaction in a simple ratio by volume, provided that all gases are at the same temperature and pressure.

29. (a) Yes

(b) According to the law of multiple proportions

(c) $H_2 + O_2 \rightarrow H_2O$

$2\ g \quad 16\ g \quad 18\ g$

(c) $H_2 + O_2 \rightarrow H_2O_2$

$2\ g \quad 32\ g \quad 34\ g$

Here masses of oxygen, (i.e., 16 g in H_2O and 32 g in H_2O_2) which combine with fixed mass of hydrogen (2 g) are in the simple ratio i.e., 16 : 32 or 1 : 2

30. $$\text{Average Atomic Mass} = \frac{\{(\text{Natural abundance of } {}^1H \times \text{molar mass}) + (\text{Natural abundance of } {}^2H \times \text{molar mass of } {}^2H)\}}{100}$$

$$= \frac{99.985 \times 1 + 0.015 \times 2}{100}$$

$$= \frac{99.985 + 0.030}{100} = \frac{100.015}{100} = 1.00015\ u$$

31. From the equation, 63.5 g of zinc liberates 22.7 litre of hydrogen. So 32.65 g of zinc will liberate

$$32.65\ g\ Zn \times \frac{22.7\ L\ H_2}{65.3\ g\ Zn} = \frac{22.7}{2} L = 11.35\ L$$

32. 3 molal solution of NaOH means that 3 mols of NaOH are dissolved in 1000 g of solvent.

$\therefore$ Mass of Solution = Mass of Solvent + Mass of Solute

$$= 1000\ g + (3 \times 40\ g) = 1120\ g$$

$$\text{Volume of Solution} = \frac{1120}{1.110}\ mL = 1009.00\ mL$$

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(Since density of solution = 1.110g mL^{-1})

Since 1009 mL solution contains 3 mols of NaOH

$$\therefore \text{ Molarity } = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litre}}$$

$$= \frac{3 \text{ mol}}{1009.00} \times 1000 = 2.97 \text{ M}$$

33. No, Molality of solution does not change with temperature since mass remains unaffected with temperature.

34. Mass of NaOH = 4 g

$$\text{Number of moles of NaOH} = \frac{4 \text{ g}}{40 \text{ g}} = 0.1 \text{ mol}$$

Mass of H_2O = 36 g

$$\text{Number of moles of } H_2O = \frac{36 \text{ g}}{18 \text{ g}} = 2 \text{ mol}$$

$$\text{Mole fraction of water} = \frac{\text{Number of moles of } H_2O}{\text{No. of moles of water + No. of moles of NaOH}}$$

$$= \frac{2}{2 + 0.1} = \frac{2}{2.1} = 0.95$$

$$\text{Mole fraction of NaOH} = \frac{\text{Number of moles of NaOH}}{\text{No. of moles of NaOH + No. of moles of water}}$$

$$= \frac{0.1}{2 + 0.1} = \frac{0.1}{2.1} = 0.047$$

Mass of solution = mass of water + mass of NaOH = 36 g + 4 g = 40 g

Volume of solution = 40 × 1 = 40 mL

(Since specific gravity of solution is = 1 g mL^{-1})

$$\text{Molarity of solution} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litre}}$$

$$= \frac{0.1 \text{ mol NaOH}}{0.04 \text{ L}} = 2.5 \text{ M}$$

35. $2A + 4B \rightarrow 3C + 4D$

According to the above equation, 2 mols of 'A' require 4 mols of 'B' for the reaction.

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Hence, for 5 mols of 'A', the moles of 'B' required = $5 \text{ mol of A} \times \frac{4 \text{ mol of B}}{2 \text{ mol of A}}$

$= 10 \text{ mol B}$

But we have only 6 mols of 'B', hence, 'B' is the limiting reagent. So amount of 'C' formed is determined by amount of 'B'.

Since 4 mols of 'B' give 3 mols of 'C'. Hence 6 mols of 'B' will give

$$6 \text{ mol of B} \times \frac{3 \text{ mol of C}}{4 \text{ mol of B}} = 4.5 \text{ mol of C}$$

IV. Matching Type

36. (i) → (b) (ii) → (c) (iii) → (a) (iv) → (e)
(v) → (d)

37. (i) → (e) (ii) → (d) (iii) → (b) (iv) → (g)
(v) → (c), (h) (vi) → (f) (vii) → (a) (viii) → (i)

V. Assertion and Reason Type

38. (i) 39. (ii) 40. (iii) 41. (iii)

VI. Long Answer Type

42. (i) p_1=1 atm, T_1=273 K, V_1=?

32 g of oxygen occupies 22.4 L of volume at STP*

Hence, 1.6 g of oxygen will occupy, $1.6 \text{ g oxygen} \times \frac{22.4 \text{ L}}{32 \text{ g oxygen}} = 1.12 \text{ L}$

V_1=1.12 L

$p_2 = \frac{p_1}{2} = \frac{1}{2} = 0.5$ atm.

V_2=?

According to Boyle's law :

$p_1V_1 = p_2V_2$

$V_2 = \frac{p_1 \times V_1}{p_2} = \frac{1 \text{ atm.} \times 1.12 \text{ L}}{0.5 \text{ atm.}} = 2.24 \text{ L}$

* Old STP conditions 273.15 K, 1 atm, volume occupied by 1 mol of gas = 22.4 L.
New STP conditions 273.15 K, 1 bar, volume occupied by a gas = 22.7 L.

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(ii) Number of molecules of oxygen in the vessel = $\frac{6.022 \times 10^{23} \times 1.6}{32}$

$= 3.011 \times 10^{22}$

43. Number of moles of HCl = 250 mL × $\frac{0.76\ M}{1000}$ = 0.19 mol

Mass of $CaCO_3$ = 1000 g

Number of moles of $CaCO_3$ = $\frac{1000\ g}{100\ g}$ = 10 mol

According to given equation 1 mol of $CaCO_3$ (s) requires 2 mol of HCl (aq). Hence, for the reaction of 10 mol of $CaCO_3$ (s) number of moles of HCl required would be:

$$10 \text{ mol } CaCO_3 \times \frac{2 \text{ mol HCl (aq)}}{1 \text{ mol } CaCO_3 \text{ (s)}} = 20 \text{ mol HCl (aq)}$$

But we have only 0.19 mol HCl (aq), hence, HCl (aq) is limiting reagent.

So amount of $CaCl_2$ formed will depend on the amount of HCl available.

Since, 2 mol HCl (aq) forms 1 mol of $CaCl_2$, therefore, 0.19 mol of HCl (aq) would give:

$$0.19 \text{ mol HCl (aq)} \times \frac{1 \text{ mol } CaCl_2 \text{ (aq)}}{2 \text{ mol HCl (aq)}} = 0.095 \text{ mol}$$

or $0.095 \times$ molar mass of $CaCl_2 = 0.095 \times 111 = 10.54$ g

45. (**Hint :** Show that the masses of B which combine with the fixed mass of A in different combinations are related to each other by simple whole numbers).

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Unit

2

STRUCTURE OF ATOM

I. Multiple Choice Questions (Type-I)

1. Which of the following conclusions could not be derived from Rutherford's α-particle scattering experiement?

(i) Most of the space in the atom is empty.

(ii) The radius of the atom is about 10^{-10} m while that of nucleus is 10^{-15} m.

(iii) Electrons move in a circular path of fixed energy called orbits.

(iv) Electrons and the nucleus are held together by electrostatic forces of attraction.

2. Which of the following options does not represent ground state electronic configuration of an atom?

(i) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$

(ii) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9\ 4s^2$

(iii) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

(iv) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

3. The probability density plots of 1s and 2s orbitals are given in Fig. 2.1:

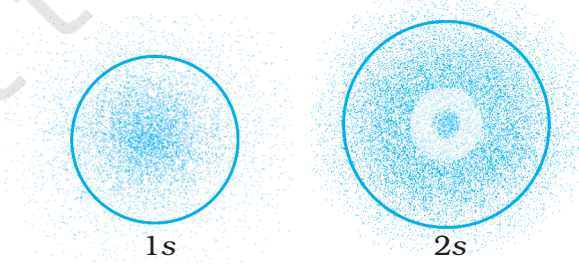

Fig. *2.1*

The density of dots in a region represents the probability density of finding electrons in the region.

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On the basis of above diagram which of the following statements is incorrect?

(i) 1*s* and 2*s* orbitals are spherical in shape.

(ii) The probability of finding the electron is maximum near the nucleus.

(iii) The probability of finding the electron at a given distance is equal in all directions.

(iv) The probability density of electrons for 2*s* orbital decreases uniformly as distance from the nucleus increases.

4. Which of the following statement is **not** correct about the characteristics of cathode rays?

(i) They start from the cathode and move towards the anode.

(ii) They travel in straight line in the absence of an external electrical or magnetic field.

(iii) Characteristics of cathode rays do not depend upon the material of electrodes in cathode ray tube.

(iv) Characteristics of cathode rays depend upon the nature of gas present in the cathode ray tube.

5. Which of the following statements about the electron is incorrect?

(i) It is a negatively charged particle.

(ii) The mass of electron is equal to the mass of neutron.

(iii) It is a basic constituent of all atoms.

(iv) It is a constituent of cathode rays.

6. Which of the following properties of atom could be explained correctly by Thomson Model of atom?

(i) Overall neutrality of atom.

(ii) Spectra of hydrogen atom.

(iii) Position of electrons, protons and neutrons in atom.

(iv) Stability of atom.

7. Two atoms are said to be isobars if.

(i) they have same atomic number but different mass number.

(ii) they have same number of electrons but different number of neutrons.

(iii) they have same number of neutrons but different number of electrons.

(iv) sum of the number of protons and neutrons is same but the number of protons is different.

8. The number of radial nodes for 3*p* orbital is _____.

(i) 3

(ii) 4

(iii) 2

(iv) 1

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9. Number of angular nodes for 4*d* orbital is _____.

(i) 4

(ii) 3

(iii) 2

(iv) 1

10. Which of the following is responsible to rule out the existence of definite paths or trajectories of electrons?

(i) Pauli's exclusion principle.

(ii) Heisenberg's uncertainty principle.

(iii) Hund's rule of maximum multiplicity.

(iv) Aufbau principle.

11. Total number of orbitals associated with third shell will be _____.

(i) 2

(ii) 4

(iii) 9

(iv) 3

12. Orbital angular momentum depends on _____.

(i) *l*

(ii) *n* and *l*

(iii) *n* and *m*

(iv) *m* and *s*

13. Chlorine exists in two isotopic forms, Cl-37 and Cl-35 but its atomic mass is 35.5. This indicates the ratio of Cl-37 and Cl-35 is approximately

(i) 1:2

(ii) 1:1

(iii) 1:3

(iv) 3:1

14. The pair of ions having same electronic configuration is _____.

(i) Cr^{3+}, Fe^{3+}

(ii) Fe^{3+}, Mn^{2+}

(iii) Fe^{3+}, Co^{3+}

(iv) Sc^{3+}, Cr^{3+}

15. For the electrons of oxygen atom, which of the following statements is correct?

(i) Z_{eff} for an electron in a 2*s* orbital is the same as Z_{eff} for an electron in a 2*p* orbital.

(ii) An electron in the 2*s* orbital has the same energy as an electron in the 2*p* orbital.

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(iii) Z_{eff} for an electron in 1*s* orbital is the same as Z_{eff} for an electron in a 2*s* orbital.

(iv) The two electrons present in the 2*s* orbital have spin quantum numbers m_s but of opposite sign.

16. If travelling at same speeds, which of the following matter waves have the shortest wavelength?

(i) Electron

(ii) Alpha particle (He^{2+})

(iii) Neutron

(iv) Proton

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

17. Identify the pairs which are **not** of isotopes?

(i) ${}^{12}_{6}X$, ${}^{13}_{6}Y$

(ii) ${}^{35}_{17}X$, ${}^{37}_{17}Y$

(iii) ${}^{14}_{6}X$, ${}^{14}_{7}Y$

(iv) ${}^{8}_{4}X$, ${}^{8}_{5}Y$

18. Out of the following pairs of electrons, identify the pairs of electrons present in degenerate orbitals :

(i) (a) $n = 3,\ l = 2,\ m_l = -2,\ m_s = -\frac{1}{2}$

(b) $n = 3,\ l = 2,\ m_l = -1,\ m_s = -\frac{1}{2}$

(ii) (a) $n = 3,\ l = 1,\ m_l = 1,\ m_s = +\frac{1}{2}$

(b) $n = 3,\ l = 2,\ m_l = 1,\ m_s = +\frac{1}{2}$

(iii) (a) $n = 4,\ l = 1,\ m_l = 1,\ m_s = +\frac{1}{2}$

(b) $n = 3,\ l = 2,\ m_l = 1,\ m_s = +\frac{1}{2}$

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(iv) (a) $n = 3,\ l = 2,\ m_l = +2,\ m_s = -\frac{1}{2}$

(b) $n = 3,\ l = 2,\ m_l = +2,\ m_s = +\frac{1}{2}$

19. Which of the following sets of quantum numbers are correct?

	n	l	m_l
(i)	1	1	+2
(ii)	2	1	+1
(iii)	3	2	–2
(iv)	3	4	–2

20. In which of the following pairs, the ions are iso-electronic?

(i) Na^+, Mg^{2+}

(ii) Al^{3+}, O^-

(iii) Na^+, O^{2-}

(iv) N^{3-}, Cl^-

21. Which of the following statements concerning the quantum numbers are correct?

(i) Angular quantum number determines the three dimensional shape of the orbital.

(ii) The principal quantum number determines the orientation and energy of the orbital.

(iii) Magnetic quantum number determines the size of the orbital.

(iv) Spin quantum number of an electron determines the orientation of the spin of electron relative to the chosen axis.

III. Short Answer Type

22. Arrange *s*, *p* and *d* sub-shells of a shell in the increasing order of effective nuclear charge (Z_{eff}) experienced by the electron present in them.

23. Show the distribution of electrons in oxygen atom (atomic number 8) using orbital diagram.

24. Nickel atom can lose two electrons to form Ni^{2+} ion. The atomic number of nickel is 28. From which orbital will nickel lose two electrons.

25. Which of the following orbitals are degenerate?

$3d_{xy}, 4d_{xy} 3d_{z^2}, 3d_{yz}, 4d_{yz}, 4d_{z^2}$

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26. Calculate the total number of angular nodes and radial nodes present in 3*p* orbital.

27. The arrangement of orbitals on the basis of energy is based upon their $(n+l)$ value. Lower the value of $(n+l)$, lower is the energy. For orbitals having same values of $(n+l)$, the orbital with lower value of n will have lower energy.

I. Based upon the above information, arrange the following orbitals in the increasing order of energy.

(a) 1*s*, 2*s*, 3*s*, 2*p*

(b) 4*s*, 3*s*, 3*p*, 4*d*

(c) 5*p*, 4*d*, 5*d*, 4*f*, 6*s*

(d) 5*f*, 6*d*, 7*s*, 7*p*

II. Based upon the above information, solve the questions given below :

(a) Which of the following orbitals has the lowest energy?

4*d*, 4*f*, 5*s*, 5*p*

(b) Which of the following orbitals has the highest energy?

5*p*, 5*d*, 5*f*, 6*s*, 6*p*

28. Which of the following will not show deflection from the path on passing through an electric field?

Proton, cathode rays, electron, neutron.

29. An atom having atomic mass number 13 has 7 neutrons. What is the atomic number of the atom?

30. Wavelengths of different radiations are given below :

λ(A) = 300 nm λ(B) = 300 μm λ(C) = 3 nm λ(D) = 30 A^0

Arrange these radiations in the increasing order of their energies.

31. The electronic configuration of valence shell of Cu is $3d^{10}4s^1$ and not $3d^9 4s^2$. How is this configuration explained?

32. The Balmer series in the hydrogen spectrum corresponds to the transition from $n_1 = 2$ to $n_2 = 3, 4, \ldots\ldots$. This series lies in the visible region. Calculate the wave number of line associated with the transition in Balmer series when the electron moves to $n = 4$ orbit.

($R_H = 109677\ cm^{-1}$)

33. According to de Broglie, matter should exhibit dual behaviour, that is both particle and wave like properties. However, a cricket ball of mass 100 g does not move like a wave when it is thrown by a bowler at a speed of 100 km/h. Calculate the wavelength of the ball and explain why it does not show wave nature.

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34. What is the experimental evidence in support of the idea that electronic energies in an atom are quantized?

35. Out of electron and proton which one will have, a higher velocity to produce matter waves of the same wavelength? Explain it.

36. A hypothetical electromagnetic wave is shown in Fig. 2.2. Find out the wavelength of the radiation.

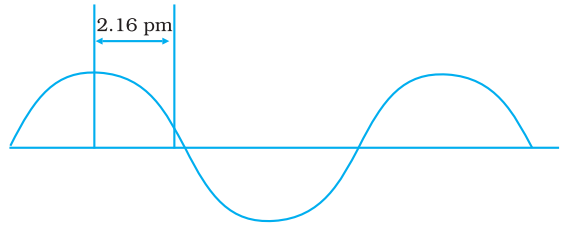

Fig. 2.2

37. Chlorophyll present in green leaves of plants absorbs light at 4.620×10^{14} Hz. Calculate the wavelength of radiation in nanometer. Which part of the electromagnetic spectrum does it belong to?

38. What is the difference between the terms orbit and orbital?

39. Table-tennis ball has a mass 10 g and a speed of 90 m/s. If speed can be measured within an accuracy of 4% what will be the uncertainty in speed and position?

40. The effect of uncertainty principle is significant only for motion of microscopic particles and is negligible for the macroscopic particles. Justify the statement with the help of a suitable example.

41. Hydrogen atom has only one electron, so mutual repulsion between electrons is absent. However, in multielectron atoms mutual repulsion between the electrons is significant. How does this affect the energy of an electron in the orbitals of the same principal quantum number in multielectron atoms?

IV. Matching Type

In some of the following questions, one option of left column may be correlated to more than one option in the right column.

42. Match the following species with their corresponding ground state electronic configuration.

	Atom / Ion		Electronic configuration
(i)	Cu	(a)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$
(ii)	Cu^{2+}	(b)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$

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(iii) Zn^{2+} (c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

(iv) Cr^{3+} (d) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

(e) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

43. Match the quantum numbers with the information provided by these.

	Quantum number		**Information provided**
(i)	Principal quantum number	(a)	orientation of the orbital
(ii)	Azimuthal quantum number	(b)	energy and size of orbital
(iii)	Magnetic quantum number	(c)	spin of electron
(iv)	Spin quantum number	(d)	shape of the orbital

44. Match the following rules with their statements :

	Rules		**Statements**
(i)	Hund's Rule	(a)	No two electrons in an atom can have the same set of four quantum numbers.
(ii)	Aufbau Principle	(b)	Half-filled and completely filled orbitals have extra stablity.
(iii)	Pauli Exclusion Principle	(c)	Pairing of electrons in the orbitals belonging to the same subshell does not take place until each orbital is singly occupied.
(iv)	Heisenberg's Uncertainty Principle	(d)	It is impossible to determine the exact position and exact momentum of a subatomic particle simultaneously.
		(e)	In the ground state of atoms, orbitals are filled in the order of their increasing energies.

45. Match the following

(i) X-rays (a) $\nu = 10^0 - 10^4\ Hz$

(ii) UV (b) $\nu = 10^{10}\ Hz$

(iii) Long radio waves (c) $\nu = 10^{16}\ Hz$

(iv) Microwave (d) $\nu = 10^{18}\ Hz$

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46. Match the following

(i)	Photon	(a)	Value is 4 for N shell
(ii)	Electron	(b)	Probability density
(iii)	ψ^2	(c)	Always positive value
(iv)	Principal quantum number n	(d)	Exhibits both momentum and wavelength

47. Match species given in Column I with the electronic configuration given in Column II.

Column I		Column II	
(i)	Cr	(a)	$[Ar]3d^8 4s^0$
(ii)	Fe^{2+}	(b)	$[Ar]3d^{10} 4s^1$
(iii)	Ni^{2+}	(c)	$[Ar]3d^6 4s^0$
(iv)	Cu	(d)	$[Ar]\ 3d^5 4s^1$
		(e)	$[Ar]3d^6 4s^2$

V. Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

48. ***Assertion (A) :*** All isotopes of a given element show the same type of chemical behaviour.

Reason (R) : The chemical properties of an atom are controlled by the number of electrons in the atom.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

49. ***Assertion (A) :*** Black body is an ideal body that emits and absorbs radiations of all frequencies.

Reason (R) : The frequency of radiation emitted by a body goes from a lower frequency to higher frequency with an increase in temperature.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true but R is not the explanation of A.

(iii) A is true and R is false.

(iv) Both A and R are false.

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50. ***Assertion (A) :*** It is impossible to determine the exact position and exact momentum of an electron simultaneously.

Reason (R) : The path of an electron in an atom is clearly defined.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true and R is not the correct explanation of A.

(iii) A is true and R is false.

(iv) Both A and R are false.

VI. Long Answer Type

51. What is photoelectric effect? State the result of photoelectric effect experiment that could not be explained on the basis of laws of classical physics. Explain this effect on the basis of quantum theory of electromagnetic radiations.

52. Threshold frequency, ν_0 is the minimum frequency which a photon must possess to eject an electron from a metal. It is different for different metals. When a photon of frequency $1.0\times10^{15}\ s^{-1}$ was allowed to hit a metal surface, an electron having 1.988×10^{-19} J of kinetic energy was emitted. Calculate the threshold frequency of this metal. Show that an electron will not be emitted if a photon with a wavelength equal to 600 nm hits the metal surface.

53. When an electric discharge is passed through hydrogen gas, the hydrogen molecules dissociate to produce excited hydrogen atoms. These excited atoms emit electromagnetic radiation of discrete frequencies which can be given by the general formula

$$\bar{\nu} = 109677\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

What points of Bohr's model of an atom can be used to arrive at this formula? Based on these points derive the above formula giving description of each step and each term.

54. Calculate the energy and frequency of the radiation emitted when an electron jumps from $n = 3$ to $n = 2$ in a hydrogen atom.

55. Why was a change in the Bohr Model of atom required? Due to which important development (s), concept of movement of an electron in an orbit was replaced by, the concept of probability of finding electron in an orbital? What is the name given to the changed model of atom?

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ANSWERS

I. Multiple Choice Questions (Type-I)

1. (iii) 2. (ii) 3. (iv) 4. (iv) 5. (ii) 6. (i)

7. (iv) 8. (iv) 9. (iii) 10. (ii) 11. (iii) 12. (i)

13. (iii) 14. (ii) 15. (iv) 16. (ii)

II. Multiple Choice Questions (Type-II)

17. (iii), (iv) 18. (i), (iv) 19. (ii), (iii)

20. (i), (iii) 21. (i), (iv)

III. Short Answer Type

22. $d < p < s$

23.

24. $4s$

25. $3d_{xy}$, $3d_{z^2}$, $3d_{yz}$ and $4d_{xy}$, $4d_{yz}$, $4d_{z^2}$

26. For $3p$ orbital $n = 3$, $l = 1$
Number of angular nodes = $l = 1$
Number of radial nodes = $n - l - 1 = 3-1-1=1$

27. I. (a) $1s < 2s < 2p < 3s$ II. (a) $5s$ (b) $5f$
(b) $3s < 3p < 4s < 4d$
(c) $4d < 5p < 6s < 4f < 5d$
(d) $7s < 5f < 6d < 7p$

28. neutron

29. A = 13, A – Z = 7 $\therefore$ Z = 6
atomic number = 6

30. B < A < C = D

Hint : $E \alpha \frac{1}{\lambda}$

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31. Completely filled and half filled orbitals have extra stability. In $3d^{10}4s^1$, d orbital is completely filled and s is half filled. So it is more stable configuration.

32. $\bar{\nu} = 109677\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right] \text{cm}^{-1}$

For $n_i = 2$ to $n_f = 4$ transition in Balmer series.

$\therefore \quad \bar{\nu} = 109677\left(\frac{1}{2^2} - \frac{1}{4^2}\right) \text{cm}^{-1}$

$= 109677\left(\frac{1}{4} - \frac{1}{16}\right) \text{cm}^{-1} = 20564.44 \text{ cm}^{-1}$

33. $\lambda = \frac{h}{mv}$

m = 100 g = 0.1 kg.

v = 100 km/hr $= \frac{100 \times 1000 \text{ m}}{60 \times 60 \text{ s}} = \frac{1000}{36} \text{ms}^{-1}$

$h = 6.626 \times 10^{-34}$ Js

$\lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{0.1 \text{ kg} \times \frac{1000}{36} \text{ ms}^{-1}} = 6.626 \times 10^{-36} \times 36 \text{ m}^{-1} = 238.5 \times 10^{-36} \text{m}^{-1}$

Since the wavelength is very small, the wave nature cannot be detected.

35. Being lighter particles, electrons will have higher velocity.

Hint : $\left(\lambda = \frac{h}{mv}\right)$

36. Wavelength is the distance between two successive peaks or two successive troughs of a wave. So $\lambda = 4 \times 2.16 \text{ pm} = 8.64 \text{ pm}$

37. $\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{4.620 \times 10^{14} \text{ Hz}} = 0.6494 \times 10^{-6} \text{ m} = 649.4 \text{ nm}$; Visible light.

39. Uncertainty in the speed of ball $= \frac{90 \times 4}{100} = \frac{360}{100} = 3.6 \text{ ms}^{-1}$

Uncertainty in position $= \frac{h}{4\pi m \Delta v}$

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$$= \frac{6.626 \times 10^{-34}\,\text{Js}}{4 \times 3.14 \times 10 \times 10^{-3}\,\text{kg g}^{-1} \times 3.6\ \text{ms}^{-1}}$$

$$= 1.46 \times 10^{-33}\ \text{m}$$

41. The energy of electron is determined by the value of n in hydrogen atom and by $n + l$ in multielectron atom. So for a given principal quantum number electrons of s, p, d and f orbitals have different energy.

IV. Matching Type

42. (i) → (c) (ii) → (d) (iii) → (a) (iv) → (e)

43. (i) → (b) (ii) → (d) (iii) → (a) (iv) → (c)

44. (i) → (c) (ii) → (e) (iii) → (a) (iv) → (d)

45. (i) → (d) (ii) → (c) (iii) → (a) (iv) → (b)

46. (i) → (d) (ii) → (d) (iii) → (b), (c) (iv) → (a), (c)

47. (i) → (d) (ii) → (c) (iii) → (a) (iv) → (b)

V. Assertion and Reason Type

48. (i) 49. (ii) 50. (iii)

VI. Long Answer Type

52. $\left(\textbf{Hint :}\ h\nu = h\nu_0 + \frac{1}{2}\text{mv}^2\right)$

54. $\Delta E = -3.052 \times 10^{-19}$ J, $\nu = 4.606 \times 10^{16}$ Hz

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Unit

3

Classification of Elements and Periodicity in Properties

I. Multiple Choice Questions (Type-I)

1. Consider the isoelectronic species, Na^+, Mg^{2+}, F^- and O^{2-}. The correct order of increasing length of their radii is _____.

(i) $F^- < O^{2-} < Mg^{2+} < Na^+$

(ii) $Mg^{2+} < Na^+ < F^- < O^{2-}$

(iii) $O^{2-} < F^- < Na^+ < Mg^{2+}$

(iv) $O^{2-} < F^- < Mg^{2+} < Na^+$

2. Which of the following is not an actinoid?

(i) Curium (Z = 96)

(ii) Californium (Z = 98)

(iii) Uranium (Z = 92)

(iv) Terbium (Z = 65)

3. The order of screening effect of electrons of s, p, d and f orbitals of a given shell of an atom on its outer shell electrons is:

(i) $s > p > d > f$

(ii) $f > d > p > s$

(iii) $p < d < s > f$

(iv) $f > p > s > d$

4. The first ionisation enthalpies of Na, Mg, Al and Si are in the order:

(i) Na < Mg > Al < Si

(ii) Na > Mg > Al > Si

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(iii) Na < Mg < Al < Si

(iv) Na > Mg > Al < Si

5. The electronic configuration of gadolinium (Atomic number 64) is

(i) [Xe] $4f^3\ 5d^5\ 6s^2$

(ii) [Xe] $4f^7\ 5d^2\ 6s^1$

(iii) [Xe] $4f^7\ 5d^1\ 6s^2$

(iv) [Xe] $4f^8\ 5d^6\ 6s^2$

6. The statement that is **not** correct for periodic classification of elements is:

(i) The properties of elements are periodic function of their atomic numbers.

(ii) Non metallic elements are less in number than metallic elements.

(iii) For transition elements, the 3*d*-orbitals are filled with electrons after 3*p*-orbitals and before 4*s*-orbitals.

(iv) The first ionisation enthalpies of elements generally increase with increase in atomic number as we go along a period.

7. Among halogens, the correct order of amount of energy released in electron gain (electron gain enthalpy) is:

(i) F > Cl > Br > I

(ii) F < Cl < Br < I

(iii) F < Cl > Br > I

(iv) F < Cl < Br < I

8. The period number in the long form of the periodic table is equal to

(i) magnetic quantum number of any element of the period.

(ii) atomic number of any element of the period.

(iii) maximum Principal quantum number of any element of the period.

(iv) maximum Azimuthal quantum number of any element of the period.

9. The elements in which electrons are progressively filled in 4*f*-orbital are called

(i) actinoids

(ii) transition elements

(iii) lanthanoids

(iv) halogens

10. Which of the following is the correct order of size of the given species:

(i) $I > I^- > I^+$

(ii) $I^+ > I^- > I$

(iii) $I > I^+ > I^-$

(iv) $I^- > I > I^+$

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11. The formation of the oxide ion, O^{2-} (g), from oxygen atom requires first an exothermic and then an endothermic step as shown below:

$O(g) + e^- \longrightarrow O^-(g)$; $\Delta H^\ominus = -141$ kJ mol^{-1}

$O^-(g) + e^- \longrightarrow O^{2-}(g)$; $\Delta H^\ominus = +780$ kJ mol^{-1}

Thus process of formation of O^{2-} in gas phase is unfavourable even though O^{2-} is isoelectronic with neon. It is due to the fact that,

(i) oxygen is more electronegative.

(ii) addition of electron in oxygen results in larger size of the ion.

(iii) electron repulsion outweighs the stability gained by achieving noble gas configuration.

(iv) O^- ion has comparatively smaller size than oxygen atom.

12. Comprehension given below is followed by some multiple choice questions. Each question has one correct option. Choose the correct option.

In the modern periodic table, elements are arranged in order of increasing atomic numbers which is related to the electronic configuration. Depending upon the type of orbitals receiving the last electron, the elements in the periodic table have been divided into four blocks, viz, *s*, *p*, *d* and *f*. The modern periodic table consists of 7 periods and 18 groups. Each period begins with the filling of a new energy shell. In accordance with the Arfbau principle, the seven periods (1 to 7) have 2, 8, 8, 18, 18, 32 and 32 elements respectively. The seventh period is still incomplete. To avoid the periodic table being too long, the two series of *f*-block elements, called lanthanoids and actinoids are placed at the bottom of the main body of the periodic table.

(a) The element with atomic number 57 belongs to

(i) *s*-block

(ii) *p*-block

(iii) *d*-block

(iv) *f*-block

(b) The last element of the *p*-block in 6th period is represented by the outermost electronic configuration.

(i) $7s^2\ 7p^6$

(ii) $5f^{14}\ 6d^{10}\ 7s^2\ 7p^0$

(iii) $4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$

(iv) $4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$

(c) Which of the elements whose atomic numbers are given below, cannot be accommodated in the present set up of the long form of the periodic table?

(i) 107

(ii) 118

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(iii) 126

(iv) 102

(d) The electronic configuration of the element which is just above the element with atomic number 43 in the same group is _____.

(i) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$

(ii) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^3\ 4p^6$

(iii) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

(iv) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$

(e) The elements with atomic numbers 35, 53 and 85 are all _____.

(i) noble gases

(ii) halogens

(iii) heavy metals

(iv) light metals

13. Electronic configurations of four elements A, B, C and D are given below :

(A) $1s^2\ 2s^2\ 2p^6$ (B) $1s^2\ 2s^2\ 2p^4$

(C) $1s^2\ 2s^2\ 2p^6\ 3s^1$ (D) $1s^2\ 2s^2\ 2p^5$

Which of the following is the correct order of increasing tendency to gain electron :

(i) A < C < B < D

(ii) A < B < C < D

(iii) D < B < C < A

(iv) D < A < B < C

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

14. Which of the following elements can show covalency greater than 4?

(i) Be

(ii) P

(iii) S

(iv) B

15. Those elements impart colour to the flame on heating in it, the atoms of which require low energy for the ionisation (i.e., absorb energy in the visible region of spectrum). The elements of which of the following groups will impart colour to the flame?

(i) 2

(ii) 13

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(iii) 1

(iv) 17

16. Which of the following sequences contain atomic numbers of only representative elements?

(i) 3, 33, 53, 87

(ii) 2, 10, 22, 36

(iii) 7, 17, 25, 37, 48

(iv) 9, 35, 51, 88

17. Which of the following elements will gain one electron more readily in comparison to other elements of their group?

(i) S (g)

(ii) Na (g)

(iii) O (g)

(iv) Cl (g)

18. Which of the following statements are correct?

(i) Helium has the highest first ionisation enthalpy in the periodic table.

(ii) Chlorine has less negative electron gain enthalpy than fluorine.

(iii) Mercury and bromine are liquids at room temperature.

(iv) In any period, atomic radius of alkali metal is the highest.

19. Which of the following sets contain only isoelectronic ions?

(i) Zn^{2+}, Ca^{2+}, Ga^{3+}, Al^{3+}

(ii) K^{+}, Ca^{2+}, Sc^{3+}, Cl^{-}

(iii) P^{3-}, S^{2-}, Cl^{-}, K^{+}

(iv) Ti^{4+}, Ar, Cr^{3+}, V^{5+}

20. In which of the following options order of arrangement does **not** agree with the variation of property indicated against it?

(i) $Al^{3+} < Mg^{2+} < Na^{+} < F^{-}$ (increasing ionic size)

(ii) B < C < N < O (increasing first ionisation enthalpy)

(iii) I < Br < Cl < F (increasing electron gain enthalpy)

(iv) Li < Na < K < Rb (increasing metallic radius)

21. Which of the following have no unit?

(i) Electronegativity

(ii) Electron gain enthalpy

(iii) Ionisation enthalpy

(iv) Metallic character

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22. Ionic radii vary in

(i) inverse proportion to the effective nuclear charge.

(ii) inverse proportion to the square of effective nuclear charge.

(iii) direct proportion to the screening effect.

(iv) direct proportion to the square of screening effect.

23. An element belongs to 3rd period and group-13 of the periodic table. Which of the following properties will be shown by the element?

(i) Good conductor of electricity

(ii) Liquid, metallic

(iii) Solid, metallic

(iv) Solid, non metallic

III. Short Answer Type

24. Explain why the electron gain enthalpy of fluorine is less negative than that of chlorine.

25. All transition elements are *d*-block elements, but all *d*-block elements are not transition elements. Explain.

26. Identify the group and valency of the element having atomic number 119. Also predict the outermost electronic configuration and write the general formula of its oxide.

27. Ionisation enthalpies of elements of second period are given below :

Ionisation enthalpy/ k cal mol^{-1} : 520, 899, 801, 1086, 1402, 1314, 1681, 2080.

Match the correct enthalpy with the elements and complete the graph given in Fig. 3.1. Also write symbols of elements with their atomic number.

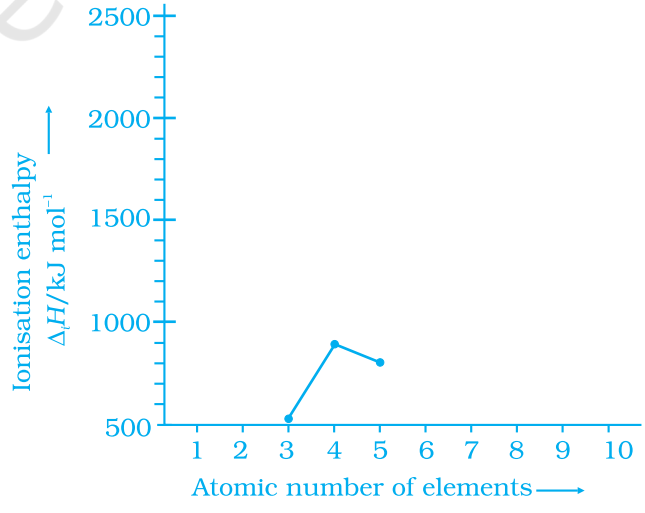

Fig. *3.1*

28. Among the elements B, Al, C and Si,

(i) which element has the highest first ionisation enthalpy?

(ii) which element has the most metallic character?

Justify your answer in each case.

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29. Write four characteristic properties of *p*-block elements.

30. Choose the correct order of atomic radii of fluorine and neon (in pm) out of the options given below and justify your answer.

(i) 72, 160

(ii) 160, 160

(iii) 72, 72

(iv) 160, 72

31. Illustrate by taking examples of transition elements and non-transition elements that oxidation states of elements are largely based on electronic configuration.

32. Nitrogen has positive electron gain enthalpy whereas oxygen has negative. However, oxygen has lower ionisation enthalpy than nitrogen. Explain.

33. First member of each group of representative elements (i.e., *s* and *p*-block elements) shows anomalous behaviour. Illustrate with two examples.

34. *p*-Block elements form acidic, basic and amphoteric oxides. Explain each property by giving two examples and also write the reactions of these oxides with water.

35. How would you explain the fact that first ionisation enthalpy of sodium is lower than that of magnesium but its second ionisation enthalpy is higher than that of magnesium?

36. What do you understand by exothermic reaction and endothermic reaction? Give one example of each type.

37. Arrange the elements N, P, O and S in the order of-

(i) increasing first ionisation enthalpy.

(ii) increasing non metallic character.

Give reason for the arrangement assigned.

38. Explain the deviation in ionisation enthalpy of some elements from the general trend by using Fig. 3.2.

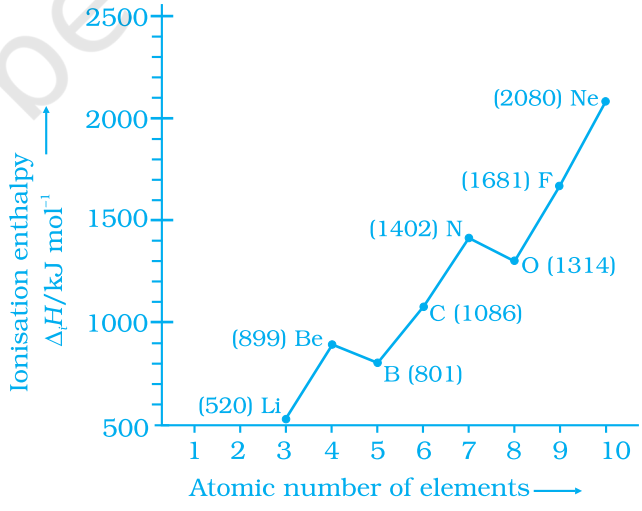

***Fig.** 3.2*

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39. Explain the following:

(a) Electronegativity of elements increase on moving from left to right in the periodic table.

(b) Ionisation enthalpy decrease in a group from top to bottom?

40. How does the metallic and non metallic character vary on moving from left to right in a period?

41. The radius of Na^+ cation is less than that of Na atom. Give reason.

42. Among alkali metals which element do you expect to be least electronegative and why?

IV. Matching Type

43. Match the correct atomic radius with the element.

Element	Atomic radius (pm)
Be	74
C	88
O	111
B	77
N	66

44. Match the correct ionisation enthalpies and electron gain enthalpies of the following elements.

	Elements		ΔH_1	ΔH_2	$\Delta_{eg} H$
(i)	Most reactive non metal	A.	419	3051	– 48
(ii)	Most reactive metal	B.	1681	3374	– 328
(iii)	Least reactive element	C.	738	1451	– 40
(iv)	Metal forming binary halide	D.	2372	5251	+ 48

45. Electronic configuration of some elements is given in Column I and their electron gain enthalpies are given in Column II. Match the electronic configuration with electron gain enthalpy.

Column (I)		Column (II)	
Electronic configuration		**Electron gain enthalpy/kJ mol^{-1}**	
(i)	$1s^2\ 2s^2\ sp^6$	(A)	– 53
(ii)	$1s^2\ 2s^2\ 2p^6\ 3s^1$	(B)	– 328
(iii)	$1s^2\ 2s^2\ 2p^5$	(C)	– 141
(iv)	$1s^2\ 2s^2\ 2p^4$	(D)	+ 48

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V. Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of reason (R) is given. Choose the correct option out of the choices given below each question.

46. ***Assertion (A) :*** Generally, ionisation enthalpy increases from left to right in a period.

Reason (R) : When successive electrons are added to the orbitals in the same principal quantum level, the shielding effect of inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus.

(i) Assertion is correct statement and reason is wrong statement.

(ii) Assertion and reason both are correct statements and reason is correct explanation of assertion.

(iii) Assertion and reason both are wrong statements.

(iv) Assertion is wrong statement and reason is correct statement.

47. ***Assertion (A) :*** Boron has a smaller first ionisation enthalpy than beryllium.

Reason (R) : The penetration of a 2*s* electron to the nucleus is more than the 2*p* electron hence 2*p* electron is more shielded by the inner core of electrons than the 2*s* electrons.

(i) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(ii) Assertion is correct statement but reason is wrong statement.

(iii) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(iv) Assertion and reason both are wrong statements.

48. ***Assertion (A) :*** Electron gain enthalpy becomes less negative as we go down a group.

Reason (R) : Size of the atom increases on going down the group and the added electron would be farther from the nucleus.

(i) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(ii) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(iii) Assertion and reason both are wrong statements.

(iv) Assertion is wrong statement but reason is correct statement.

VI. Long Answer Type

49. Discuss the factors affecting electron gain enthalpy and the trend in its variation in the periodic table.

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50. Define ionisation enthalpy. Discuss the factors affecting ionisation enthalpy of the elements and its trends in the periodic table.

51. Justify the given statement with suitable examples— "the Properties of the elements are a periodic function of their atomic numbers".

52. Write down the outermost electronic configuration of alkali metals. How will you justify their placement in group 1 of the periodic table?

53. Write the drawbacks in Mendeleev's periodic table that led to its modification.

54. In what manner is the long form of periodic table better than Mendeleev's periodic table? Explain with examples.

55. Discuss and compare the trend in ionisation enthalpy of the elements of group1 with those of group17 elements.

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ANSWERS

I. Multiple Choice Questions (Type-I)

1. (ii) 2. (iv) 3. (i) 4. (i) 5. (iii) 6. (iii)

7. (iii) 8. (iii) 9. (iii) 10. (iv) 11. (iii)

12.(a) (iii), (b) (iii), (c) (iii), (d) (i), (e) (ii) 13. (i)

II. Multiple Choice Questions (Type-II)

14. (ii), (iii) 15. (i), (iii) 16. (i), (iv)

17. (i), (iv) 18. (i), (iii), (iv) 19. (ii), (iii)

20. (ii), (iii) 21. (i), (iv) 22. (i), (iii)

23. (i), (iii)

III. Short Answer Type

24. The added electron in fluorine goes to second quantum level. Due to small size of fluorine it experiences repulsion from other electrons much more in comparison to that in chlorine because in chlorine, the electron is added to 3rd quantum level in which larger space is available for movement.

26. Group : 1, Valency : 1

Outermost electronic configuration = $8s^1$

Formula of Oxide = M_2O

27. Compare your plot with the plot given in the textbook.

28. (i) Carbon

(ii) Aluminium

30. (i)

32. The outermost electronic configuraton of nitrogen ($2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$) is very stable because *p*-orbital is half filled. Addition of extra electron to any of the 2*p* orbital requires energy.

Oxygen has 4 electrons in 2*p* orbitals and acquires stable configuration i.e., $2p^3$ configuration after removing one electron.

35. After removing 1 electron from the sodium atom the ion formed acquires the configuration of inert gas, neon. The second electron is removed from one of the 2*p*-orbitals which are completely filled i.e., have a total of 6 electrons and are closer to the nucleus.

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37. (i) S < P < N < O

(ii) P < S < N < O

39. (a) Decrease in size of atom and increase in nuclear charge.

(b) Increase in atomic size.

40. Metallic character decreases and non metallic character increases in moving from left to right in a period. It is due to increase in ionisation enthalpy and electron gain enthalpy.

41. Decrease of one shell.

42. Electronegativity decreases in a group from top to bottom. Thus, caesium is the least electronegative element.

IV. Matching Type

43. Be = 111, O = 66, C = 77, B = 88, N = 74.

44. Most reactive non metal = B, Most reactive metal = A, Least reactive element = D, Metal forming binary halide = C

45. (i) $\longrightarrow$ (D); (ii) $\longrightarrow$ (A) (iii) $\longrightarrow$ (B) (iv) $\longrightarrow$ (C)

V. Assertion and Reason Type

46. (ii)

47. (iii)

48. (iv)

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Unit

4

CHEMICAL BONDING AND MOLECULAR STRUCTURE

I. Multiple Choice Questions (Type-I)

1. Isostructural species are those which have the same shape and hybridisation. Among the given species identify the isostructural pairs.

(i) [NF_3 and BF_3]

(ii) [BF_4^- and NH_4^+]

(iii) [BCl_3 and $BrCl_3$]

(iv) [NH_3 and NO_3^-]

2. Polarity in a molecule and hence the dipole moment depends primarily on electronegativity of the constituent atoms and shape of a molecule. Which of the following has the highest dipole moment?

(i) CO_2

(ii) HI

(iii) H_2O

(iv) SO_2

3. The types of hybrid orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are expected to be

(i) *sp*, sp^3 and sp^2

(ii) *sp*, sp^2 and sp^3

(iii) sp^2, *sp* and sp^3

(iv) sp^2, sp^3 and *sp*

4. Hydrogen bonds are formed in many compounds e.g., H_2O, HF, NH_3. The boiling point of such compounds depends to a large extent on the strength of hydrogen bond and the number of hydrogen bonds. The correct decreasing order of the boiling points of above compounds is :

(i) HF > H_2O > NH_3

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(ii) $H_2O > HF > NH_3$

(iii) $NH_3 > HF > H_2O$

(iv) $NH_3 > H_2O > HF$

5. In PO_4^{3-} ion the formal charge on the oxygen atom of P–O bond is

(i) + 1

(ii) – 1

(iii) – 0.75

(iv) + 0.75

6. In NO_3^- ion, the number of bond pairs and lone pairs of electrons on nitrogen atom are

(i) 2, 2

(ii) 3, 1

(iii) 1, 3

(iv) 4, 0

7. Which of the following species has tetrahedral geometry?

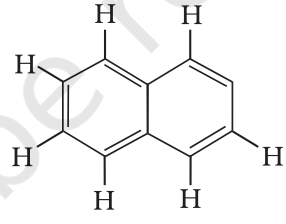
(i) BH_4^-

(ii) NH_2^-

(iii) CO_3^{2-}

(iv) H_3O^+

8. Number of π bonds and σ bonds in the following structure is–



(i) 6, 19

(ii) 4, 20

(iii) 5, 19

(iv) 5, 20

9. Which molecule/ion out of the following does **not** contain unpaired electrons?

(i) N_2^+

(ii) O_2

(iii) O_2^{2-}

(iv) B_2

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10. In which of the following molecule/ion all the bonds are **not** equal?

(i) XeF_4

(ii) BF_4^-

(iii) C_2H_4

(iv) SiF_4

11. In which of the following substances will hydrogen bond be strongest?

(i) HCl

(ii) H_2O

(iii) HI

(iv) H_2S

12. If the electronic configuration of an element is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$, the four electrons involved in chemical bond formation will be_____.

(i) $3p^6$

(ii) $3p^6$, $4s^2$

(iii) $3p^6$, $3d^2$

(iv) $3d^2$, $4s^2$

13. Which of the following angle corresponds to sp^2 hybridisation?

(i) 90°

(ii) 120°

(iii) 180°

(iv) 109°

The electronic configurations of three elements, A, B and C are given below. Answer the questions 14 to 17 on the basis of these configurations.

A	$1s^2$	$2s^2$	$2p^6$		
B	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^3$
C	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^5$

14. Stable form of **A** may be represented by the formula :

(i) A

(ii) A_2

(iii) A_3

(iv) A_4

15. Stable form of **C** may be represented by the formula :

(i) C

(ii) C_2

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(iii) C_3

(iv) C_4

16. The molecular formula of the compound formed from B and C will be

(i) BC

(ii) B_2C

(iii) BC_2

(iv) BC_3

17. The bond between B and C will be

(i) Ionic

(ii) Covalent

(iii) Hydrogen

(iv) Coordinate

18. Which of the following order of energies of molecular orbitals of N_2 is correct?

(i) $(\pi 2p_y) < (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$

(ii) $(\pi 2p_y) > (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$

(iii) $(\pi 2p_y) < (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$

(iv) $(\pi 2p_y) > (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$

19. Which of the following statement is **not** correct from the view point of molecular orbital theory?

(i) Be_2 is not a stable molecule.

(ii) He_2 is not stable but He_2^+ is expected to exist.

(iii) Bond strength of N_2 is maximum amongst the homonuclear diatomic molecules belonging to the second period.

(iv) The order of energies of molecular orbitals in N_2 molecule is

$\sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

20. Which of the following options represents the correct bond order :

(i) $O_2^- > O_2 > O_2^+$

(ii) $O_2^- < O_2 < O_2^+$

(iii) $O_2^- > O_2 < O_2^+$

(iv) $O_2^- < O_2 > O_2^+$

21. The electronic configuration of the outer most shell of the most electronegative element is

(i) $2s^2 2p^5$

(ii) $3s^2 3p^5$

(iii) $4s^2 4p^5$

(iv) $5s^2 5p^5$

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22. Amongst the following elements whose electronic configurations are given below, the one having the highest ionisation enthalpy is

(i) $[Ne]3s^2 3p^1$

(ii) $[Ne]3s^2 3p^3$

(iii) $[Ne]3s^2 3p^2$

(iv) $[Ar]3d^{10} 4s^2 4p^3$

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

23. Which of the following have identical bond order?

(i) CN^-

(ii) NO^+

(iii) O_2^-

(iv) O_2^{2-}

24. Which of the following attain the linear structure:

(i) $BeCl_2$

(ii) NCO^+

(iii) NO_2

(iv) CS_2

25. CO is isoelectronic with

(i) NO^+

(ii) N_2

(iii) $SnCl_2$

(iv) NO_2^-

26. Which of the following species have the same shape?

(i) CO_2

(ii) CCl_4

(iii) O_3

(iv) NO_2^-

27. Which of the following statements are correct about CO_3^{2-}?

(i) The hybridisation of central atom is sp^3.

(ii) Its resonance structure has one C–O single bond and two C=O double bonds.

(iii) The average formal charge on each oxygen atom is 0.67 units.

(iv) All C–O bond lengths are equal.

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28. Dimagnetic species are those which contain no unpaired electrons. Which among the following are dimagnetic?

(i) N_2

(ii) N_2^{2-}

(iii) O_2

(iv) O_2^{2-}

29. Species having same bond order are :

(i) N_2

(ii) N_2^-

(iii) F_2^+

(iv) O_2^-

30. Which of the following statements are **not** correct?

(i) NaCl being an ionic compound is a good conductor of electricity in the solid state.

(ii) In canonical structures there is a difference in the arrangement of atoms.

(iii) Hybrid orbitals form stronger bonds than pure orbitals.

(iv) VSEPR Theory can explain the square planar geometry of XeF_4.

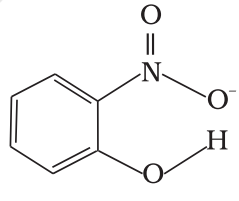
III. Short Answer Type

31. Explain the non linear shape of H_2S and non planar shape of PCl_3 using valence shell electron pair repulsion theory.

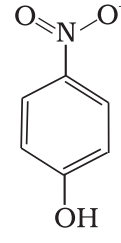
32. Using molecular orbital theory, compare the bond energy and magnetic character of O_2^+ and O_2^- species.

33. Explain the shape of BrF_5.

34. Structures of molecules of two compounds are given below :



(I)



(II)

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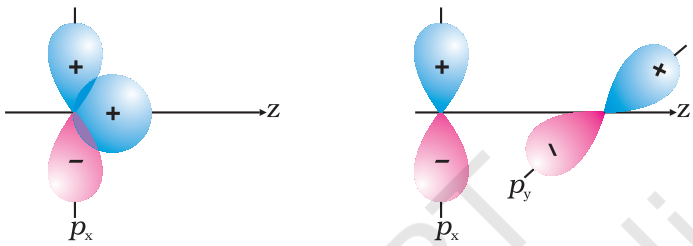
(a) Which of the two compounds will have intermolecular hydrogen bonding and which compound is expected to show intramolecular hydrogen bonding.

(b) The melting point of a compound depends on, among other things, the extent of hydrogen bonding. On this basis explain which of the above two compounds will show higher melting point.

(c) Solubility of compounds in water depends on power to form hydrogen bonds with water. Which of the above compounds will form hydrogen bond with water easily and be more soluble in it.

35. Why does type of overlap given in the following figure not result in bond formation?



36. Explain why PCl_5 is trigonal bipyramidal whereas IF_5 is square pyramidal.

37. In both water and dimethyl ether ($CH_3 — \ddot{O} — CH_3$), oxygen atom is central atom, and has the same hybridisation, yet they have different bond angles. Which one has greater bond angle? Give reason.

38. Write Lewis structure of the following compounds and show formal charge on each atom.

HNO_3, NO_2, H_2SO_4

39. The energy of $\sigma 2p_z$ molecular orbital is greater than $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals in nitrogen molecule. Write the complete sequence of energy levels in the increasing order of energy in the molecule. Compare the relative stability and the magnetic behaviour of the following species :

N_2, N_2^+, N_2^-, N_2^{2+}

40. What is the effect of the following processes on the bond order in N_2 and O_2?

(i) $N_2 \rightarrow N_2^+ + e^-$ (ii) $O_2 \rightarrow O_2^+ + e^-$

41. Give reasons for the following :

(i) Covalent bonds are directional bonds while ionic bonds are non-directional.

(ii) Water molecule has bent structure whereas carbon dioxide molecule is linear.

(iii) Ethyne molecule is linear.

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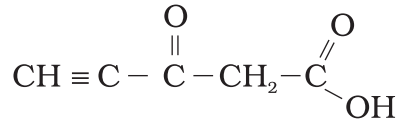
42. What is an ionic bond? With two suitable examples explain the difference between an ionic and a covalent bond?

43. Arrange the following bonds in order of increasing ionic character giving reason.

N—H, F—H, C—H and O—H

44. Explain why CO_3^{2-} ion cannot be represented by a single Lewis structure. How can it be best represented?

45. Predict the hybridisation of each carbon in the molecule of organic compound given below. Also indicate the total number of sigma and pi bonds in this molecule.



46. Group the following as linear and non-linear molecules :

H_2O, HOCl, $BeCl_2$, Cl_2O

47. Elements X, Y and Z have 4, 5 and 7 valence electrons respectively. (i) Write the molecular formula of the compounds formed by these elements individually with hydrogen. (ii) Which of these compounds will have the highest dipole moment?

48. Draw the resonating structure of

(i) Ozone molecule

(ii) Nitrate ion

49. Predict the shapes of the following molecules on the basis of hybridisation.

BCl_3, CH_4, CO_2, NH_3

50. All the C—O bonds in carbonate ion (CO_3^{2-}) are equal in length. Explain.

51. What is meant by the term average bond enthalpy? Why is there difference in bond enthalpy of O—H bond in ethanol (C_2H_5OH) and water?

IV. Matching Type

52. Match the species in Column I with the type of hybrid orbitals in Column II.

Column I		Column II	
(i)	SF_4	(a)	sp^3d^2
(ii)	IF_5	(b)	d^2sp^3
(iii)	NO_2^+	(c)	sp^3d
(iv)	NH_4^+	(d)	sp^3
		(e)	sp

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53. Match the species in Column I with the geometry/shape in Column II.

	Column I	**Column II**
(i)	H_3O^+	(a) Linear
(ii)	$HC \equiv CH$	(b) Angular
(iii)	ClO_2^-	(c) Tetrahedral
(iv)	NH_4^+	(d) Trigonal bipyramidal
		(e) Pyramidal

54. Match the species in Column I with the bond order in Column II.

	Column I	**Column II**
(i)	NO	(a) 1.5
(ii)	CO	(b) 2.0
(iii)	O_2^-	(c) 2.5
(iv)	O_2	(d) 3.0

55. Match the items given in Column I with examples given in Column II.

	Column I	**Column II**
(i)	Hydrogen bond	(a) C
(ii)	Resonance	(b) LiF
(iii)	Ionic solid	(c) H_2
(iv)	Covalent solid	(d) HF
		(e) O_3

56. Match the shape of molecules in Column I with the type of hybridisation in Column II.

	Column I	**Column II**
(i)	Tetrahedral	(a) sp^2
(ii)	Trigonal	(b) sp
(iii)	Linear	(c) sp^3

V. Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

57. ***Assertion (A) :*** Sodium chloride formed by the action of chlorine gas on sodium metal is a stable compound.

Reason (R) : This is because sodium and chloride ions acquire octet in sodium chloride formation.

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(i) A and R both are correct, and R is the correct explanation of A.

(ii) A and R both are correct, but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) A and R both are false.

58. ***Assertion (A) :*** Though the central atom of both NH_3 and H_2O molecules are sp^3 hybridised, yet H–N–H bond angle is greater than that of H–O–H.

Reason (R) : This is because nitrogen atom has one lone pair and oxygen atom has two lone pairs.

(i) A and R both are correct, and R is the correct explanation of A.

(ii) A and R both are correct, but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) A and R both are false.

59. ***Assertion (A):*** Among the two O–H bonds in H_2O molecule, the energy required to break the first O–H bond and the other O–H bond is the same.

Reason (R) : This is because the electronic environment around oxygen is the same even after breakage of one O–H bond.

(i) A and R both are correct, and R is correct explanation of A.

(ii) A and R both are correct, but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) A and R both are false.

VI. Long Answer Type

60. (i) Discuss the significance/ applications of dipole moment.

(ii) Represent diagrammatically the bond moments and the resultant dipole moment in CO_2 , NF_3 and $CHCl_3$.

61. Use the molecular orbital energy level diagram to show that N_2 would be expected to have a triple bond, F_2, a single bond and Ne_2, no bond.

62. Briefly describe the valence bond theory of covalent bond formation by taking an example of hydrogen. How can you interpret energy changes taking place in the formation of dihydrogen?

63. Describe hybridisation in the case of PCl_5 and SF_6. The axial bonds are longer as compared to equatorial bonds in PCl_5 whereas in SF_6 both axial bonds and equatorial bonds have the same bond length. Explain.

64. (i) Discuss the concept of hybridisation. What are its different types in a carbon atom.

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(ii) What is the type of hybridisation of carbon atoms marked with star.

(a) $\overset{*}{C}H_2 = CH - \overset{O}{\overset{\|}{\overset{*}{C}}} - O - H$

(b) $CH_3 - \overset{*}{C}H_2 - OH$

(c) $CH_3 - CH_2 - \overset{O}{\overset{\|}{\overset{*}{C}}} - H$

(d) $\overset{*}{C}H_3 - CH = CH - CH_3$

(e) $CH_3 - \overset{*}{C} \equiv CH$

Comprehension given below is followed by some multiple choice questions. Each question has one correct option. Choose the correct option.

Molecular orbitals are formed by the overlap of atomic orbitals. Two atomic orbitals combine to form two molecular orbitals called bonding molecular orbital (BMO) and anti bonding molecular orbital (ABMO). Energy of anti bonding orbital is raised above the parent atomic orbitals that have combined and the energy of the bonding orbital is lowered than the parent atomic orbitals. Energies of various molecular orbitals for elements hydrogen to nitrogen increase in the order : $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x \approx \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x \approx \pi^* 2p_y) < \sigma^* 2p_z$ and for oxygen and fluorine order of energy of molecular orbitals is given below : $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x \approx \pi 2p_y) < (\pi^* 2p_x \approx \pi^* 2p_y) < \sigma^* 2p_z$ Different atomic orbitals of one atom combine with those atomic orbitals of the second atom which have comparable energies and proper orientation. Further, if the overlapping is head on, the molecular orbital is called 'Sigma', (σ) and if the overlap is lateral, the molecular orbital is called 'pi', (π). The molecular orbitals are filled with electrons according to the same rules as followed for filling of atomic orbitals. However, the order for filling is not the same for all molecules or their ions. Bond order is one of the most important parameters to compare the strength of bonds.

65. Which of the following statements is correct?

(i) In the formation of dioxygen from oxygen atoms 10 molecular orbitals will be formed.

(ii) All the molecular orbitals in the dioxygen will be completely filled.

(iii) Total number of bonding molecular orbitals will not be same as total number of anti bonding orbitals in dioxygen.

(iv) Number of filled bonding orbitals will be same as number of filled anti bonding orbitals.

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66. Which of the following molecular orbitals has maximum number of nodal planes?

(i) σ^*1s

(ii) σ^*2p_z

(iii) $\pi 2p_x$

(iv) π^*2p_y

67. Which of the following pair is expected to have the same bond order?

(i) O_2, N_2

(ii) O_2^+, N_2^-

(iii) O_2^-, N_2^+

(iv) O_2^-, N_2^-

68. In which of the following molecules, $\sigma 2p_z$ molecular orbital is filled after $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals?

(i) O_2

(ii) Ne_2

(iii) N_2

(iv) F_2

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ANSWERS

I. Multiple Choice Questions (Type-I)

1. (ii)	2. (iii)	3. (ii)	4. (ii)	5. (ii)	6. (iv)
7. (i)	8. (iii)	9. (iii)	10. (iii)	11. (ii)	12. (iv)
13. (ii)	14. (i)	15. (ii)	16. (iv)	17. (ii)	18. (i)
19. (iv)	20. (ii)	21. (i)	22. (ii)		

II. Multiple Choice Questions (Type-II)

23. (i), (ii)	24. (i), (iv)	25. (i), (ii)
26. (iii), (iv)	27. (iii), (iv)	28. (i), (iv)
29. (iii), (iv)	30. (i), (ii)	

III. Short Answer Type

32. (i) According to molecular orbital theory electronic configurations of O_2^+ and O_2^- species are as follows :

O_2^+ : $(\sigma 1s)^2\ (\overset{*}{\sigma} 1s^2)(\sigma 2s)^2(\overset{*}{\sigma} 2s^2)\ (\sigma 2p_z)^2\ (\pi 2p_x^2, \pi 2p_y^2)\ (\pi^* 2p_x^1)$

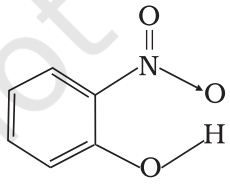
O_2^- : $(\sigma 1s)^2\ (\overset{*}{\sigma} 1s^2)(\sigma 2s)^2(\overset{*}{\sigma} 2s^2)\ (\sigma 2p_z)^2\ (\pi 2p_x^2, \pi 2p_y^2)\ (\pi^* 2p_x^2, \pi^* 2p_y^1)$

$$\text{Bond order of } O_2^+ = \frac{10-5}{2} = \frac{5}{2} = 2.5$$

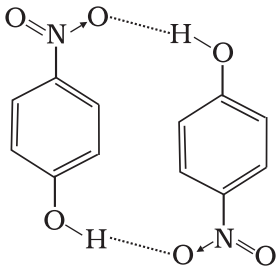
$$\text{Bond order of } O_2^- = \frac{10-7}{2} = \frac{3}{2} = 1.5$$

Higher bond order of O_2^+ shows that it is more stable than O_2^-. Both the species have unpaired electrons. So both are paramagnetic in nature.

34. (a) Compound (I) will form intramolecular hydrogen bond because NO_2 and OH group are close together in comparison to that in compound (II).



(I)



(II)

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(b) Compound (II) will have higher melting point because it forms intermolecular hydrogen bonds. Thus, more and more molecules are joined together through hydrogen bond formation.

(c) Due to intramolecular hydrogen bonding compound (I) will not be able to form hydrogen bonds with water thus will be less soluble in it while compound (II) can form hydrogen bond with water more easily and will be soluble in water.

37. [**Hint :** Dimethyl ether will have larger bond angle. There will be more repulsion between bond pairs of CH_3 groups attached in ether than between bond pairs of hydrogen atoms attached to oxygen in water. The carbon of CH_3 in ether is attached to three hydrogen atoms through σ bonds and electron pairs of these bonds add to the electronic charge density on carbon atom. Hence, repulsion between two —CH_3 groups will be more than that between two hydrogen atoms.]

IV. Matching Type

52. (i) → (c) (ii) → (a) (iii) → (e) (iv) → (d)

53. (i) → (e) (ii) → (a) (iii) → (b) (iv) → (c)

54. (i) → (c) (ii) → (d) (iii) → (a) (iv) → (b)

55. (i) → (d) (ii) → (e) (iii) → (b) (iv) → (a)

56. (i) → (c) (ii) → (a) (iii) → (b)

V. Assertion and Reason Type

57. (i) 58. (i) 59. (iv)

65. (i) 66. (ii) 67. (ii) 68. (iii)

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Unit

5

STATES OF MATTER

I. Multiple Choice Questions (Type-I)

1. A person living in Shimla observed that cooking food without using pressure cooker takes more time. The reason for this observation is that at high altitude:

(i) pressure increases
(ii) temperature decreases
(iii) pressure decreases
(iv) temperature increases

2. Which of the following property of water can be used to explain the spherical shape of rain droplets?

(i) viscosity
(ii) surface tension
(iii) critical phenomena
(iv) pressure

3. A plot of volume (V) versus temperature (T) for a gas at constant pressure is a straight line passing through the origin. The plots at different values of pressure are shown in Fig. 5.1. Which of the following order of pressure is correct for this gas?

(i) $p_1 > p_2 > p_3 > p_4$
(ii) $p_1 = p_2 = p_3 = p_4$
(iii) $p_1 < p_2 < p_3 < p_4$
(iv) $p_1 < p_2 = p_3 < p_4$

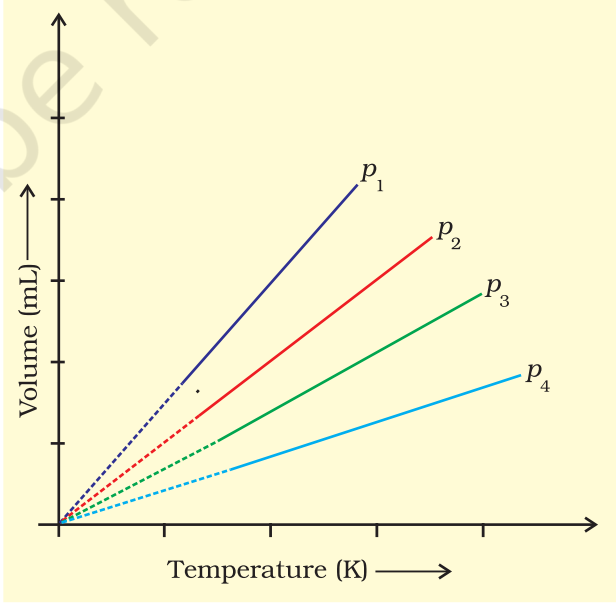

Fig. *5.1*

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4. The interaction energy of London force is inversely proportional to sixth power of the distance between two interacting particles but their magnitude depends upon

(i) charge of interacting particles

(ii) mass of interacting particles

(iii) polarisability of interacting particles

(iv) strength of permanent dipoles in the particles.

5. Dipole-dipole forces act between the molecules possessing permanent dipole. Ends of dipoles possess 'partial charges'. The partial charge is

(i) more than unit electronic charge

(ii) equal to unit electronic charge

(iii) less than unit electronic charge

(iv) double the unit electronic charge

6. The pressure of a 1:4 mixture of dihydrogen and dioxygen enclosed in a vessel is one atmosphere. What would be the partial pressure of dioxygen?

(i) 0.8×10^{5} atm

(ii) 0.008 Nm^{-2}

(iii) 8×10^{4} Nm^{-2}

(iv) 0.25 atm

7. As the temperature increases, average kinetic energy of molecules increases. What would be the effect of increase of temperature on pressure provided the volume is constant?

(i) increases

(ii) decreases

(iii) remains same

(iv) becomes half

8. Gases possess characteristic critical temperature which depends upon the magnitude of intermolecular forces between the particles. Following are the critical temperatures of some gases.

Gases	H_2	He	O_2	N_2
Critical temperature in Kelvin	33.2	5.3	154.3	126

From the above data what would be the order of liquefaction of these gases? Start writing the order from the gas liquefying first

(i) H_2, He, O_2, N_2

(ii) He, O_2, H_2, N_2

(iii) N_2, O_2, He, H_2

(iv) O_2, N_2, H_2, He

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9. What is SI unit of viscosity coefficient (η)?

(i) Pascal

(ii) Nsm^{-2}

(iii) km^{-2} s

(iv) $N\ m^{-2}$

10. Atmospheric pressures recorded in different cities are as follows:

Cities	**Shimla**	**Bangalore**	**Delhi**	**Mumbai**
p in N/m^2	1.01×10^5	1.2×10^5	1.02×10^5	1.21×10^5

Consider the above data and mark the place at which liquid will boil first.

(i) Shimla

(ii) Bangalore

(iii) Delhi

(iv) Mumbai

11. Which curve in Fig. 5.2 represents the curve of ideal gas?

(i) B only

(ii) C and D only

(iii) E and F only

(iv) A and B only

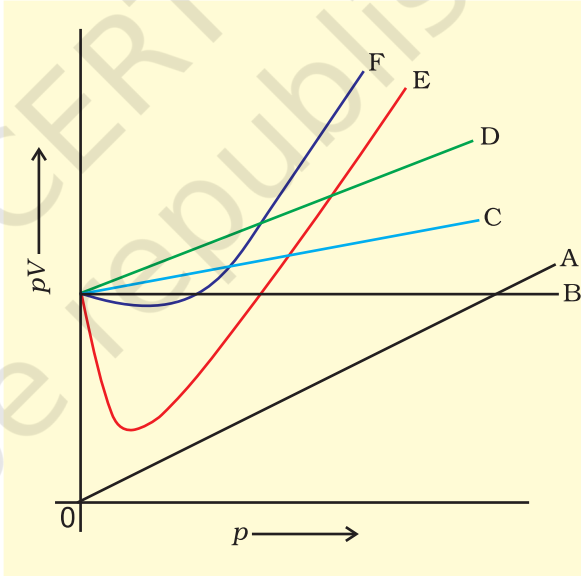

Fig. *5.2*

12. Increase in kinetic energy can overcome intermolecular forces of attraction. How will the viscosity of liquid be affected by the increase in temperature?

(i) Increase

(ii) No effect

(iii) Decrease

(iv) No regular pattern will be followed

13. How does the surface tension of a liquid vary with increase in temperature?

(i) Remains same

(ii) Decreases

(iii) Increases

(iv) No regular pattern is followed

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II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

14. With regard to the gaseous state of matter which of the following statements are correct?

(i) Complete order of molecules

(ii) Complete disorder of molecules

(iii) Random motion of molecules

(iv) Fixed position of molecules

15. Which of the following figures does **not** represent 1 mole of dioxygen gas at STP?

(i) 16 grams of gas

(ii) 22.7 litres of gas

(iii) 6.022×10^{23} dioxygen molecules

(iv) 11.2 litres of gas

16. Under which of the following two conditions applied together, a gas deviates most from the ideal behaviour?

(i) Low pressure

(ii) High pressure

(iii) Low temperature

(iv) High temperature

17. Which of the following changes decrease the vapour pressure of water kept in a sealed vessel?

(i) Decreasing the quantity of water

(ii) Adding salt to water

(iii) Decreasing the volume of the vessel to one-half

(iv) Decreasing the temperature of water

III. Short Answer Type

18. If 1 gram of each of the following gases are taken at STP, which of the gases will occupy (a) greatest volume and (b) smallest volume?

CO, H_2O, CH_4, NO

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19. Physical properties of ice, water and steam are very different. What is the chemical composition of water in all the three states.

20. The behaviour of matter in different states is governed by various physical laws. According to you what are the factors that determine the state of matter?

21. Use the information and data given below to answer the questions (a) to (c):

- Stronger intermolecular forces result in higher boiling point.
- Strength of London forces increases with the number of electrons in the molecule.
- Boiling point of HF, HCl, HBr and HI are 293 K, 189 K, 206 K and 238 K respectively.

(a) Which type of intermolecular forces are present in the molecules HF, HCl, HBr and HI?

(b) Looking at the trend of boiling points of HCl, HBr and HI, explain out of dipole-dipole interaction and London interaction, which one is predominant here.

(c) Why is boiling point of hydrogen fluoride highest while that of hydrogen chloride lowest?

22. What will be the molar volume of nitrogen and argon at 273.15K and 1 atm?

23. A gas that follows Boyle's law, Charle's law and Avogadro's law is called an ideal gas. Under what conditions a real gas would behave ideally?

24. Two different gases 'A' and 'B' are filled in separate containers of equal capacity under the same conditions of temperature and pressure. On increasing the pressure slightly the gas 'A' liquefies but gas B does not liquify even on applying high pressure until it is cooled. Explain this phenomenon.

25. Value of universal gas constant (R) is same for all gases. What is its physical significance?

26. One of the assumptions of kinetic theory of gases states that "there is no force of attraction between the molecules of a gas." How far is this statement correct? Is it possible to liquefy an ideal gas? Explain.

27. The magnitude of surface tension of liquid depends on the attractive forces between the molecules. Arrange the following in increasing order of surface tension :

water, alcohol (C_2H_5OH) and hexane [$CH_3(CH_2)_4CH_3$)].

28. Pressure exerted by saturated water vapour is called aqueous tension. What correction term will you apply to the total pressure to obtain pressure of dry gas?

29. Name the energy which arises due to motion of atoms or molecules in a body. How is this energy affected when the temperature is increased?

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30. Name two intermolecular forces that exist between HF molecules in liquid state.

31. One of the assumptions of kinetic theory of gases is that there is no force of attraction between the molecules of a gas.

State and explain the evidence that shows that the assumption is not applicable for real gases.

32. Compressibility factor, Z, of a gas is given as $Z=\frac{pV}{nRT}$

(i) What is the value of Z for an ideal gas?

(ii) For real gas what will be the effect on value of Z above Boyle's temperature?

33. The critical temperature (T_c) and critical pressure (p_c) of CO_2 are 30.98°C and 73 atm respectively. Can CO_2 (g) be liquefied at 32°C and 80 atm pressure?

34. For real gases the relation between p, V and T is given by van der Waals equation:

$$\left(p+\frac{an^2}{V^2}\right)(V-nb) = nRT$$

where 'a' and 'b' are van der Waals constants, 'nb' is approximately equal to the total volume of the molecules of a gas.

'a' is the measure of magnitude of intermolecular attraction.

(i) Arrange the following gases in the increasing order of 'b'. Give reason.

O_2, CO_2, H_2, He

(ii) Arrange the following gases in the decreasing order of magnitude of 'a'. Give reason.

CH_4, O_2, H_2

35. The relation between pressure exerted by an ideal gas (p_{ideal}) and observed pressure (p_{real}) is given by the equation

$$p_{ideal} = p_{real} + \frac{an^2}{V^2}$$

If pressure is taken in Nm^{-2}, number of moles in mol and volume in m^3, Calculate the unit of *'a'*.

What will be the unit of *'a'* when pressure is in atmosphere and volume in dm^3?

36. Name two phenomena that can be explained on the basis of surface tension.

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37. Viscosity of a liquid arises due to strong intermolecular forces existing between the molecules. Stronger the intermolecular forces, greater is the viscosity. Name the intermolecular forces existing in the following liquids and arrange them in the increasing order of their viscosities. Also give reason for the assigned order in one line.

Water, hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$), glycerine ($CH_2OH\ CH(OH)\ CH_2OH$)

38. Explain the effect of increasing the temperature of a liquid, on intermolecular forces operating between its particles, what will happen to the viscosity of a liquid if its temperature is increased?

39. The variation of pressure with volume of the gas at different temperatures can be graphically represented as shown in Fig. 5.3.

On the basis of this graph answer the following questions.

(i) How will the volume of a gas change if its pressure is increased at constant temperature?

(ii) At a constant pressure, how will the volume of a gas change if the temperature is increased from 200K to 400K?

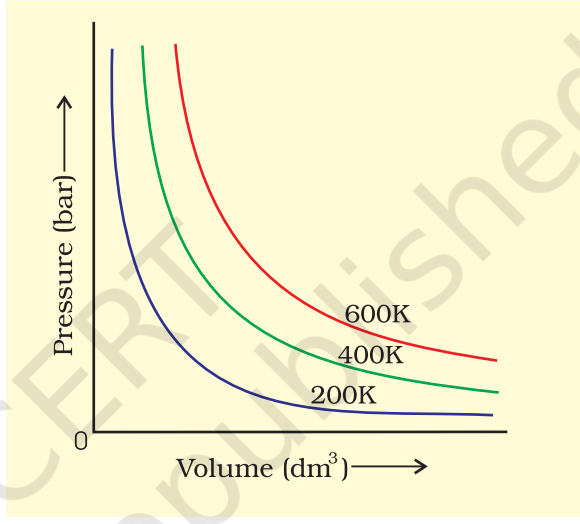

Fig. *5.3*

40. Pressure versus volume graph for a real gas and an ideal gas are shown in Fig. 5.4. Answer the following questions on the basis of this graph.

(i) Interpret the behaviour of real gas with respect to ideal gas at low pressure.

(ii) Interpret the behaviour of real gas with respect to ideal gas at high pressure.

(iii) Mark the pressure and volume by drawing a line at the point where real gas behaves as an ideal gas.

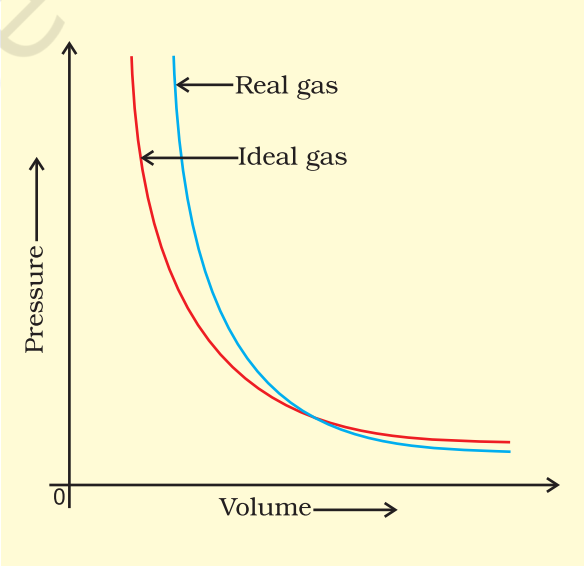

Fig. *5.4*

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IV. Matching Type

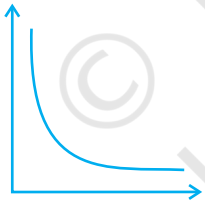
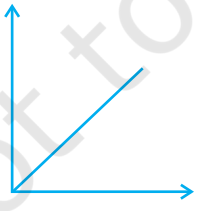
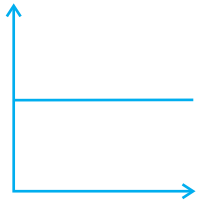
41. Match the graphs between the following variables with their names :

	Graphs		**Names**
(i)	Pressure vs temperature graph at constant molar volume.	(a)	Isotherms
(ii)	Pressure vs volume graph at constant temperature.	(b)	Constant temperature curve
(iii)	Volume vs temperature graph at constant pressure.	(c)	Isochores
		(d)	Isobars

42. Match the following gas laws with the equation representing them.

(i)	Boyle's law	(a)	$V \propto n$ at constant T and p
(ii)	Charle's law	(b)	$p_{Total} = p_1 + p_2 + p_3 + \ldots\ldots$ at constant T, V
(iii)	Dalton's law	(c)	$\frac{pV}{T}$ = Constant
(iv)	Avogadro law	(d)	$V \propto T$ at constant n and p
		(e)	$p \propto \frac{1}{V}$ at constant n and T

43. Match the following graphs of ideal gas with their co-ordinates :

	Graphical representation		***x* and *y* co-ordinates**
(i)		(a)	pV vs. V
(ii)		(b)	p vs. V
(iii)		(c)	p vs. $\frac{1}{V}$

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V. Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

44. ***Assertion (A):*** Three states of matter are the result of balance between intermolecular forces and thermal energy of the molecules.

Reason (R): Intermolecular forces tend to keep the molecules together but thermal energy of molecules tends to keep them apart.

(i) Both *A* and *R* are true and *R* is the correct explanation of *A*.

(ii) Both *A* and *R* are true but *R* is not the correct explanation of *A*.

(iii) *A* is true but *R* is false.

(iv) *A* is false but *R* is true.

45. ***Assertion (A):*** At constant temperature, pV vs V plot for real gases is not a straight line.

Reason (R) : At high pressure all gases have $Z > 1$ but at intermediate pressure most gases have $Z < 1$.

(i) Both *A* and *R* are true and *R* is the correct explanation of *A*.

(ii) Both *A* and *R* are true but *R* is not the correct explanation of *A*.

(iii) *A* is true but *R* is false.

(iv) *A* is false but *R* is true.

46. ***Assertion (A):*** The temperature at which vapour pressure of a liquid is equal to the external pressure is called boiling temperature.

Reason (R) : At high altitude atmospheric pressure is high.

(i) Both *A* and *R* are true and *R* is the correct explanation of *A*.

(ii) Both *A* and *R* are true but *R* is not the correct explanation of *A*.

(iii) *A* is true but *R* is false.

(iv) *A* is false but *R* is true.

47. ***Assertion (A):*** Gases do not liquefy above their critical temperature, even on applying high pressure.

Reason (R) : Above critical temperature, the molecular speed is high and intermolecular attractions cannot hold the molecules together because they escape because of high speed.

(i) Both *A* and *R* are true and *R* is the correct explanation of *A*.

(ii) Both *A* and *R* are true but *R* is not the correct explanation of *A*.

(iii) *A* is true but *R* is false.

(iv) *A* is false but *R* is true.

48. ***Assertion (A):*** At critical temperature liquid passes into gaseous state imperceptibly and continuously.

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Reason (R) : The density of liquid and gaseous phase is equal to critical temperature.

(i) Both *A* and *R* are true and *R* is the correct explanation of *A*.

(ii) Both *A* and *R* are true but *R* is not the correct explanation of *A*.

(iii) *A* is true but *R* is false.

(iv) *A* is false but *R* is true.

49. ***Assertion (A):*** Liquids tend to have maximum number of molecules at their surface.

Reason (R) : Small liquid drops have spherical shape.

(i) Both *A* and *R* are true and *R* is the correct explanation of *A*.

(ii) Both *A* and *R* are true but *R* is not the correct explanation of *A*.

(iii) *A* is true but *R* is false.

(iv) *A* is false but *R* is true.

VI. Long Answer Type

50. Isotherms of carbon dioxide at various temperatures are represented in Fig. 5.5. Answer the following questions based on this figure.

(i) In which state will CO_2 exist between the points *a* and *b* at temperature T_1?

(ii) At what point will CO_2 start liquefying when temperature is T_1?

(iii) At what point will CO_2 be completely liquefied when temperature is T_2.

(iv) Will condensation take place when the temperature is T_3.

(v) What portion of the isotherm at T_1 represent liquid and gaseous CO_2 at equilibrium?

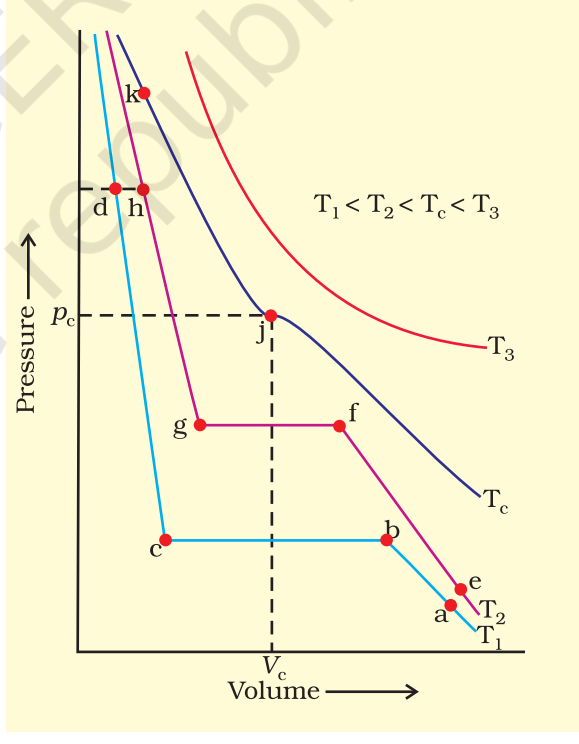

Fig. *5.5*

51. The variation of vapour pressure of different liquids with temperature is shown in Fig. 5.6.

(i) Calculate graphically boiling points of liquids A and B.

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(ii) If we take liquid C in a closed vessel and heat it continuously. At what temperature will it boil?

(iii) At high altitude, atmospheric pressure is low (say 60 mm Hg). At what temperature liquid D boils?

(iv) Pressure cooker is used for cooking food at hill station. Explain in terms of vapour pressure why is it so?

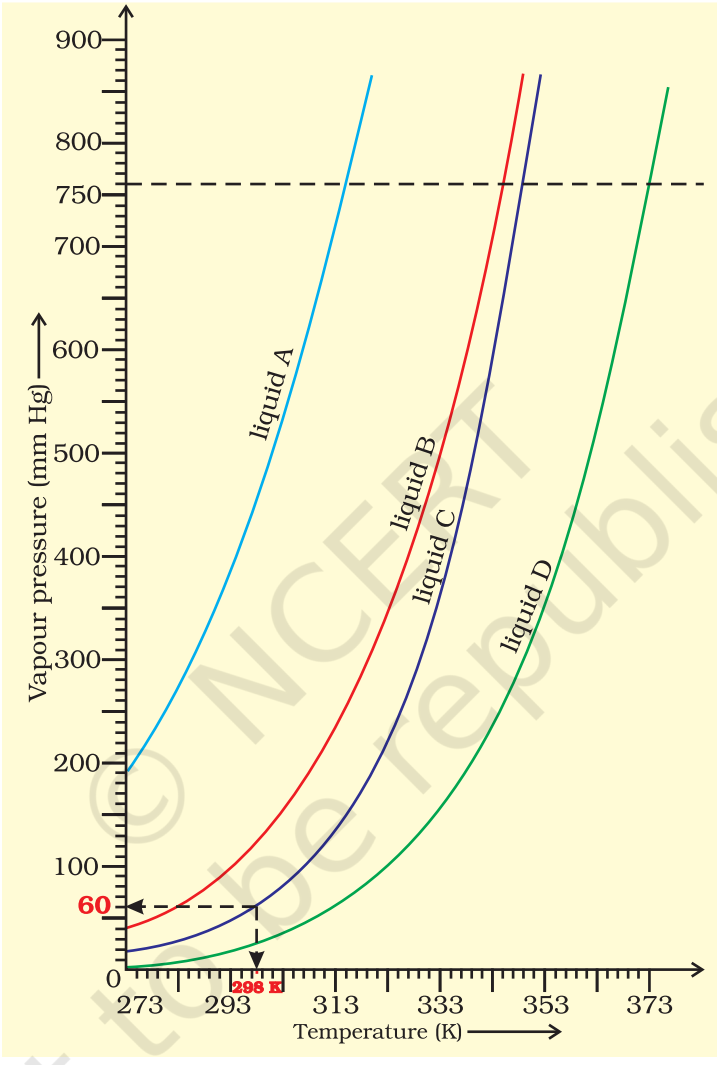

***Fig.** 5.6*

52. Why does the boundary between liquid phase and gaseous phase disappear on heating a liquid upto critical temperature in a closed vessel? In this situation what will be the state of the substance?

53. Why does sharp glass edge become smooth on heating it upto its melting point in a flame? Explain which property of liquids is responsible for this phenomenon.

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54. Explain the term 'laminar flow'. Is the velocity of molecules same in all the layers in laminar flow? Explain your answer.

55. Isotherms of carbon dioxide gas are shown in Fig. 5.7. Mark a path for changing gas into liquid such that only one phase (i.e., either a gas or a liquid) exists at any time during the change. Explain how the temperature, volume and pressure should be changed to carry out the change.

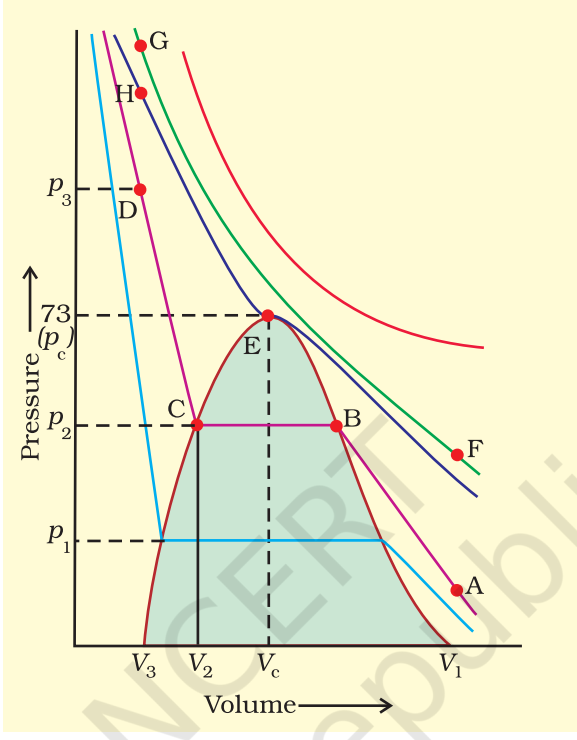

Fig. *5.7*

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ANSWERS

I. Multiple Choice Questions (Type-I)

1. (iii) 2. (ii) 3. (iii) 4. (iii) 5. (iii) 6. (iii)
7. (i) 8. (iv) 9. (ii) 10. (i) 11. (i) 12. (iii)
13. (ii)

II. Multiple Choice Questions (Type-II)

14. (ii), (iii) 15. (i), (iv) 16. (ii), (iii)
17. (ii), (iv)

III. Short Answer Type

18. a. CH_4 b. NO

19. Remains the same i.e., H_2O.

20. Pressure, temperature, mass and volume

21. (a) In HCl, HBr and HI, dipole-dipole and London forces because molecules possess permanent dipole. In HF dipole-dipole, London forces and hydrogen bonding.

    (b) Electronegativity of chlorine, bromine and iodine decreases in the order :

    $$Cl > Br > I$$

    Therefore, dipole moment should decrease from HCl to HI. Thus, dipole-dipole interaction should decrease from HCl to HI. But boiling point increases on moving from HCl to HI. This means that London forces are predominant. This is so because London forces increase as the number of electrons in a molecule increases and in this case number of electrons is increasing from HCl towards HI.

    (c) Hydrogen fluoride has highest dipole moment due to highest electronegativity of fluorine and hydrogen bonding is also present in it. Therefore, HF has highest boiling point.

22. 22.4 litre

23. Low pressure and high temperature

24. Gas 'A' is at or below its critical temperature and gas 'B' is at a temperature higher than critical temperature.

25. Unit of R depends upon those units in which p, V and T are measured, $R = \frac{pV}{nT}$. If pressure is measured in Pascal, per mole volume is measured in m^3 and temperature is measured in Kelven then. Units of 'R' are $Pam^3K^{-1}\ mol^{-1}$ or $J\ mol^{-1}\ K^{-1}$. Jule is the unit of work done so 'R' is work done per mole per kelvin.

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26. In the absence of intermolecular forces of attraction, it will not be possible to liquefy ideal gas.

27. hexane < alcohol < water

28. $P_{\text{Dry gas}} = P_{\text{Total}}$ – aqueous tension

29. Thermal energy. It is a measure of average kinetic energy of particles. It increases with increase in temperature.

30. (i) Dipole - dipole interaction
    (ii) Hydrogen - bonding

31. Real gases can be liquefied on cooling and compressing proving that forces of attraction exist between the molecules.

32. (i) $Z = 1$ for ideal gas
    (ii) For a real gas $Z > 1$ above Boyle's temperature.

33. CO_2 cannot be liquefied at 32°C by applying a pressure of 80 atm. This is because the temperature is greater than critical temperature of CO_2.

34. (i) $H_2 < He < O_2 < CO_2$ because size increases in the same order.
    (ii) $CH_4 > O_2 > H_2$ intermolecular attractions are the highest in CH_4 and lowest in H_2 because intermolecular forces increase with number of electrons in a molecule.

35. $p_{\text{ideal}} = p_{\text{real}} + \dfrac{an^2}{V^2}$

We write the known units in the above equation.

$$\text{Nm}^{-2} = \text{Nm}^{-2} + \frac{a.\ \text{mol}^2}{(\text{m}^3)^2}$$

If two values with same units are added then the units of result are same as added units.

$$\therefore \quad \text{Nm}^{-2} = \frac{a.\text{mol}^2}{\text{m}^6}$$

$$a = \frac{\text{Nm}^{-2}.\text{m}^6}{\text{mol}^2}$$

$$a = \text{Nm}^4\ \text{mol}^{-2}$$

Similarly, when p is in atm and volume in dm^3

$$a = \frac{\text{atm}(\text{dm}^3)^2}{\text{mol}^2} = \text{atm dm}^6\ \text{mol}^{-2}$$

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36. (i) Rise or fall of the liquid in a capillary - capillary action.

(ii) Spherical shape of small liquid drops.

37. In water and glycerine – Hydrogen bonding. Hexane – Dispersion forces/ London forces. The order of viscosities of these liquids is hexane < water < glycerine.

Hexane has weakest intermolecular forces and glycerine the strongest. (three OH groups). Therefore, hexane has minimum viscosity and glycerine has maximum viscosity.

38. The viscosity of a liquid decreases with the increase in temperature since the kinetic energy of the molecules can overcome intermolecular forces. So the liquid can flow more easily.

39. (1) The volume of a gas will decrease if the pressure on the gas is increased keeping the temperature constant.

(2) On increasing temperature, the volume of a gas will increase if the pressure is kept constant.

IV. Matching Type

41. (i) → (c) (ii) → (a) (iii) → (d)

42. (i) → (e) (ii) → (d) (iii) → (b) (iv)→ (a)

43. (i) → (b) (ii) → (c) (iii) → (a)

V. Assertion and Reason Type

44. (i) 45. (ii) 46. (iii) 47. (i) 48. (i) 49. (iv)

VI. Long Answer Type

50. (i) gaseous state (ii) at point b

(iii) at point g (iv) No, since $T_3 > T_c$

(v) between b and c.

51. (i) Boiling point of A = approximately 315 K, B = approximately 345 K

(ii) Will not boil

(iii) approximately 313 K

(iv) A liquid boils when vapour pressure becomes equal to the atmospheric pressure. Water boils at low temperature on hills because atmospheric pressure is low. Therefore even at low temperature vapour pressure becomes equal to atmospheric pressure.

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Unit

6

THERMODYNAMICS

I. Multiple Choice Questions (Type-I)

1. Thermodynamics is **not** concerned about_____.

(i) energy changes involved in a chemical reaction.

(ii) the extent to which a chemical reaction proceeds.

(iii) the rate at which a reaction proceeds.

(iv) the feasibility of a chemical reaction.

2. Which of the following statements is correct?

(i) The presence of reacting species in a covered beaker is an example of open system.

(ii) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.

(iii) The presence of reactants in a closed vessel made up of copper is an example of a closed system.

(iv) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.

3. The state of a gas can be described by quoting the relationship between___.

(i) pressure, volume, temperature

(ii) temperature, amount, pressure

(iii) amount, volume, temperature

(iv) pressure, volume, temperature, amount

4. The volume of gas is reduced to half from its original volume. The specific heat will be _____.

(i) reduce to half

(ii) be doubled

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(iii) remain constant

(iv) increase four times

5. During complete combustion of one mole of butane, 2658 kJ of heat is released. The thermochemical reaction for above change is

(i) $2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(l)\ \Delta_cH = -2658.0\ kJ\ mol^{-1}$

(ii) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(g)\ \Delta_cH = -1329.0\ kJ\ mol^{-1}$

(iii) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)\ \Delta_cH = -2658.0\ kJ\ mol^{-1}$

(iv) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)\ \Delta_cH = +2658.0\ kJ\ mol^{-1}$

6. $\Delta_fU^\ominus$ of formation of CH_4 (g) at certain temperature is –393 kJ mol^{-1}. The value of $\Delta_fH^\ominus$ is

(i) zero

(ii) $< \Delta_fU^\ominus$

(iii) $> \Delta_fU^\ominus$

(iv) equal to $\Delta_fU^\ominus$

7. In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following.

(i) $q = 0, \Delta T \neq 0, w = 0$

(ii) $q \neq 0, \Delta T = 0, w = 0$

(iii) $q = 0, \Delta T = 0, w = 0$

(iv) $q = 0, \Delta T < 0, w \neq 0$

8. The pressure-volume work for an ideal gas can be calculated by using the expression $w = -\int_{V_i}^{V_f} p_{ex}dV$. The work can also be calculated from the *p*V– plot by using the area under the curve within the specified limits. When an ideal gas is compressed (a) reversibly or (b) irreversibly from volume V_i to V_f. choose the correct option.

(i) w (reversible) = w (irreversible)

(ii) w (reversible) < w (irreversible)

(iii) w (reversible) > w (irreversible)

(iv) w (reversible) = w (irreversible) + $p_{ex}.\Delta V$

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9. The entropy change can be calculated by using the expression $\Delta S = \frac{q_{rev}}{T}$.

When water freezes in a glass beaker, choose the correct statement amongst the following :

(i) ΔS (system) decreases but ΔS (surroundings) remains the same.

(ii) ΔS (system) increases but ΔS (surroundings) decreases.

(iii) ΔS (system) decreases but ΔS (surroundings) increases.

(iv) ΔS (system) decreases and ΔS (surroundings) also decreases.

10. On the basis of thermochemical equations (a), (b) and (c), find out which of the algebric relationships given in options (i) to (iv) is correct.

(a) $C\ (graphite) + O_2\ (g) \longrightarrow CO_2\ (g)\ ;\ \Delta_r H = x\ kJ\ mol^{-1}$

(b) $C\ (graphite) + \frac{1}{2} O_2\ (g) \longrightarrow CO\ (g)\ ;\ \Delta_r H = y\ kJ\ mol^{-1}$

(c) $CO\ (g) + \frac{1}{2} O_2\ (g) \longrightarrow CO_2\ (g)\ ;\ \Delta_r H = z\ kJ\ mol^{-1}$

(i) $z = x + y$

(ii) $x = y - z$

(iii) $x = y + z$

(iv) $y = 2z - x$

11. Consider the reactions given below. On the basis of these reactions find out which of the algebric relations given in options (i) to (iv) is correct?

(a) $C\ (g) + 4\ H\ (g) \longrightarrow CH_4\ (g);\ \Delta_r H = x\ kJ\ mol^{-1}$

(b) $C\ (graphite,s) + 2H_2\ (g) \longrightarrow CH_4\ (g);\ \Delta_r H = y\ kJ\ mol^{-1}$

(i) $x = y$

(ii) $x = 2y$

(iii) $x > y$

(iv) $x < y$

12. The enthalpies of elements in their standard states are taken as zero. The enthalpy of formation of a compound

(i) is always negative

(ii) is always positive

(iii) may be positive or negative

(iv) is never negative

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13. Enthalpy of sublimation of a substance is equal to

(i) enthalpy of fusion + enthalpy of vapourisation

(ii) enthalpy of fusion

(iii) enthalpy of vapourisation

(iv) twice the enthalpy of vapourisation

14. Which of the following is **not** correct?

(i) ΔG is zero for a reversible reaction

(ii) ΔG is positive for a spontaneous reaction

(iii) ΔG is negative for a spontaneous reaction

(iv) ΔG is positive for a non-spontaneous reaction

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

15. Thermodynamics mainly deals with

(i) interrelation of various forms of energy and their transformation from one form to another.

(ii) energy changes in the processes which depend only on initial and final states of the microscopic systems containing a few molecules.

(iii) how and at what rate these energy transformations are carried out.

(iv) the system in equilibrium state or moving from one equilibrium state to another equilibrium state.

16. In an exothermic reaction, heat is evolved, and system loses heat to the surrounding. For such system

(i) q_p will be negative

(ii) $\Delta_r H$ will be negative

(iii) q_p will be positive

(iv) $\Delta_r H$ will be positive

17. The spontaneity means, having the potential to proceed without the assistance of external agency. The processes which occur spontaneously are

(i) flow of heat from colder to warmer body.

(ii) gas in a container contracting into one corner.

(iii) gas expanding to fill the available volume.

(iv) burning carbon in oxygen to give carbon dioxide.

18. For an ideal gas, the work of reversible expansion under isothermal condition can be calculated by using the expression $w = -nRT \ln \frac{V_f}{V_i}$

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A sample containing 1.0 mol of an ideal gas is expanded isothermally and reversibly to ten times of its original volume, in two separate experiments. The expansion is carried out at 300 K and at 600 K respectively. Choose the correct option.

(i) Work done at 600 K is 20 times the work done at 300 K.

(ii) Work done at 300 K is twice the work done at 600 K.

(iii) Work done at 600 K is twice the work done at 300 K.

(iv) $\Delta U = 0$ in both cases.

19. Consider the following reaction between zinc and oxygen and choose the correct options out of the options given below :

$2\ Zn\ (s) + O_2\ (g) \longrightarrow 2\ ZnO\ (s)$; $\Delta H = -693.8\ kJ\ mol^{-1}$

(i) The enthalpy of two moles of ZnO is less than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.

(ii) The enthalpy of two moles of ZnO is more than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.

(iii) 693.8 kJ mol^{-1} energy is evolved in the reaction.

(iv) 693.8 kJ mol^{-1} energy is absorbed in the reaction.

III. Short Answer Type

20. 18.0 g of water completely vapourises at 100°C and 1 bar pressure and the enthalpy change in the process is 40.79 kJ mol^{-1}. What will be the enthalpy change for vapourising two moles of water under the same conditions? What is the standard enthalpy of vapourisation for water?

21. One mole of acetone requires less heat to vapourise than 1 mol of water. Which of the two liquids has higher enthalpy of vapourisation?

22. Standard molar enthalpy of formation, $\Delta_f H^\ominus$ is just a special case of enthalpy of reaction, $\Delta_r H^\ominus$. Is the $\Delta_r H^\ominus$ for the following reaction same as $\Delta_f H^\ominus$? Give reason for your answer.

$CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$; $\Delta_f H^\ominus = -178.3\ kJ\ mol^{-1}$

23. The value of $\Delta_f H^\ominus$ for NH_3 is – 91.8 kJ mol^{-1}. Calculate enthalpy change for the following reaction :

$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

24. Enthalpy is an extensive property. In general, if enthalpy of an overall reaction A→B along one route is $\Delta_r H$ and $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$ ..... represent enthalpies of intermediate reactions leading to product B. What will be the relation between $\Delta_r H$ for overall reaction and $\Delta_r H_1, \Delta_r H_2$ ..... etc. for intermediate reactions.

25. The enthalpy of atomisation for the reaction $CH_4(g) \rightarrow C(g) + 4H\ (g)$ is 1665 kJ mol^{-1}. What is the bond energy of C–H bond?

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26. Use the following data to calculate $\Delta_{lattice} H^{\ominus}$ for NaBr.

$\Delta_{sub} H^{\ominus}$ for sodium metal = 108.4 kJ mol^{-1}

Ionization enthalpy of sodium = 496 kJ mol^{-1}

Electron gain enthalpy of bromine = – 325 kJ mol^{-1}

Bond dissociation enthalpy of bromine = 192 kJ mol^{-1}

$\Delta_f H^{\ominus}$ for NaBr (s) = – 360.1 kJ mol^{-1}

27. Given that $\Delta H = 0$ for mixing of two gases. Explain whether the diffusion of these gases into each other in a closed container is a spontaneous process or not?

28. Heat has randomising influence on a system and temperature is the measure of average chaotic motion of particles in the system. Write the mathematical relation which relates these three parameters.

29. Increase in enthalpy of the surroundings is equal to decrease in enthalpy of the system. Will the temperature of system and surroundings be the same when they are in thermal equilibrium?

30. At 298 K. K_p for the reaction N_2O_4 (g) $\rightleftharpoons$ $2NO_2$ (g) is 0.98. Predict whether the reaction is spontaneous or not.

31. A sample of 1.0 mol of a monoatomic ideal gas is taken through a cyclic process of expansion and compression as shown in Fig. 6.1. What will be the value of ΔH for the cycle as a whole?

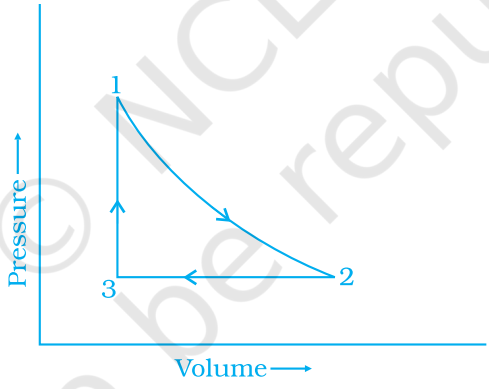

Fig. : *6.1*

32. The standard molar entropy of H_2O (l) is 70 J K^{-1} mol^{-1}. Will the standard molar entropy of H_2O(s) be more, or less than 70 J K^{-1} mol^{-1}?

33. Identify the state functions and path functions out of the following :

enthalpy, entropy, heat, temperature, work, free energy.

34. The molar enthalpy of vapourisation of acetone is less than that of water. Why?

35. Which quantity out of $\Delta_r G$ and $\Delta_r G^{\ominus}$ will be zero at equilibrium?

36. Predict the change in internal energy for an isolated system at constant volume.

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37. Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.

38. Expansion of a gas in vacuum is called free expansion. Calculate the work done and the change in internal energy when 1 litre of ideal gas expands isothermally into vacuum until its total volume is 5 litre?

39. Heat capacity (C_p) is an extensive property but specific heat (c) is an intensive property. What will be the relation between C_p and c for 1 mol of water?

40. The difference between C_P and C_V can be derived using the empirical relation $H = U + pV$. Calculate the difference between C_P and C_V for 10 moles of an ideal gas.

41. If the combustion of 1g of graphite produces 20.7 kJ of heat, what will be molar enthalpy change? Give the significance of sign also.

42. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in reactant molecules minus amount of energy required to form all the bonds in the product molecules. What will be the enthalpy change for the following reaction.

$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

Given that Bond energy of H_2, Br_2 and HBr is 435 kJ mol^{-1}, 192 kJ mol^{-1} and 368 kJ mol^{-1} respectively.

43. The enthalpy of vapourisation of CCl_4 is 30.5 kJ mol^{-1}. Calculate the heat required for the vapourisation of 284 g of CCl_4 at constant pressure. (Molar mass of CCl_4 = 154 g mol^{-1}).

44. The enthalpy of reaction for the reaction :

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ is $\Delta_r H^{\ominus} = -572$ kJ mol^{-1}.

What will be standard enthalpy of formation of H_2O (l) ?

45. What will be the work done on an ideal gas enclosed in a cylinder, when it is compressed by a constant external pressure, p_{ext} in a single step as shown in Fig. 6.2. Explain graphically.

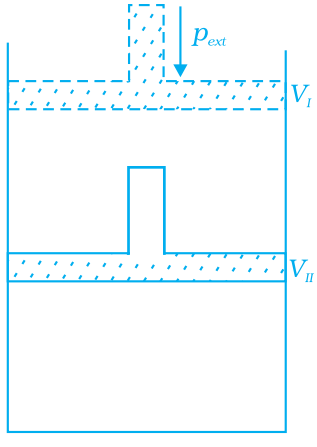

Fig. : *6.2*

46. How will you calculate work done on an ideal gas in a compression, when change in pressure is carried out in infinite steps?

47. Represent the potential energy/enthalpy change in the following processes graphically.

(a) Throwing a stone from the ground to roof.

(b) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightleftharpoons HCl(g)$ $\quad \Delta_r H^{\ominus} = -92.32$ kJ mol^{-1}

In which of the processes potential energy/enthalpy change is contributing factor to the spontaneity?

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48. Enthalpy diagram for a particular reaction is given in Fig. 6.3. Is it possible to decide spontaneity of a reaction from given diagram. Explain.

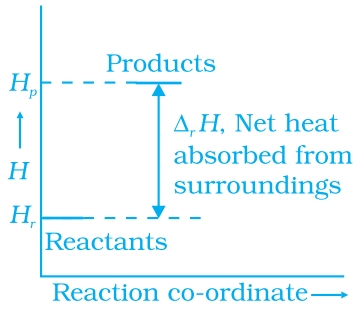

Fig. : *6.3*

49. 1.0 mol of a monoatomic ideal gas is expanded from state (1) to state (2) as shown in Fig. 6.4. Calculate the work done for the expansion of gas from state (1) to state (2) at 298 K.

50. An ideal gas is allowed to expand against a constant pressure of 2 bar from 10 L to 50 L in one step. Calculate the amount of work done by the gas. If the same expansion were carried out reversibly, will the work done be higher or lower than the earlier case?
(Given that 1 L bar = 100 J)

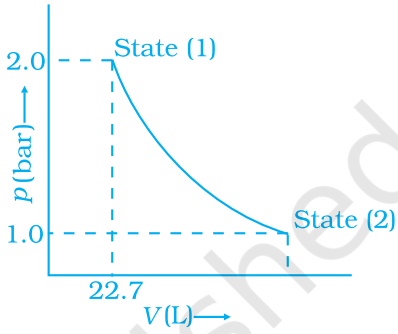

Fig. : *6.4*

IV. Matching Type

In the following questions more than one correlation is possible between options of both columns.

51. Match the following :

	A		**B**
(i)	Adiabatic process	(a)	Heat
(ii)	Isolated system	(b)	At constant volume
(iii)	Isothermal change	(c)	First law of thermodynamics
(iv)	Path function	(d)	No exchange of energy and matter
(v)	State function	(e)	No transfer of heat
(vi)	$\Delta U = q$	(f)	Constant temperature
(vii)	Law of conservation of energy	(g)	Internal energy
(viii)	Reversible process	(h)	$p_{ext} = 0$
(ix)	Free expansion	(i)	At constant pressure
(x)	$\Delta H = q$	(j)	Infinitely slow process which proceeds through a series of equilibrium states.
(xi)	Intensive property	(k)	Entropy
(xii)	Extensive property	(l)	Pressure
		(m)	Specific heat

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52. Match the following processes with entropy change:

	Reaction	Entropy change
(i)	A liquid vapourises	(a) $\Delta S = 0$
(ii)	Reaction is non-spontaneous at all temperatures and ΔH is positive	(b) ΔS = positive
(iii)	Reversible expansion of an ideal gas	(c) ΔS = negative

53. Match the following parameters with description for spontaneity :

	Δ (Parameters)			Description
	$\Delta_r H^\ominus$	$\Delta_r S^\ominus$	$\Delta_r G^\ominus$	
(i)	+	–	+	(a) Non-spontaneous at high temperature.
(ii)	–	–	+ at high T	(b) Spontaneous at all temperatures
(iii)	–	+	–	(c) Non-spontaneous at all temperatures

54. Match the following :

(i)	Entropy of vapourisation	(a)	decreases
(ii)	K for spontaneous process	(b)	is always positive
(iii)	Crystalline solid state	(c)	lowest entropy
(iv)	ΔU in adiabatic expansion of ideal gas	(d)	$\frac{\Delta H_{vap}}{T_b}$

V. Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

55. ***Assertion (A):*** Combustion of all organic compounds is an exothermic reaction.

Reason (R) : The enthalpies of all elements in their standard state are zero.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) A is false but R is true.

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56. ***Assertion (A) :*** Spontaneous process is an irreversible process and may be reversed by some external agency.

Reason (R) : Decrease in enthalpy is a contributory factor for spontaneity.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) A is false but R is true.

57. ***Assertion (A) :*** A liquid crystallises into a solid and is accompanied by decrease in entropy.

Reason (R) : In crystals, molecules organise in an ordered manner.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) A is false but R is true.

VI. Long Answer Type

58. Derive the relationship between ΔH and ΔU for an ideal gas. Explain each term involved in the equation.

59. Extensive properties depend on the quantity of matter but intensive properties do not. Explain whether the following properties are extensive or intensive.

Mass, internal energy, pressure, heat capacity, molar heat capacity, density, mole fraction, specific heat, temperature and molarity.

60. The lattice enthalpy of an ionic compound is the enthalpy when one mole of an ionic compound present in its gaseous state, dissociates into its ions. It is impossible to determine it directly by experiment. Suggest and explain an indirect method to measure lattice enthalpy of NaCl(s).

61. ΔG is net energy available to do useful work and is thus a measure of "free energy". Show mathematically that ΔG is a measure of free energy. Find the unit of ΔG. If a reaction has positive enthalpy change and positive entropy change, under what condition will the reaction be spontaneous?

62. Graphically show the total work done in an expansion when the state of an ideal gas is changed reversibly and isothermally from (p_i, V_i) to (p_f , V_f). With the help of a pV plot compare the work done in the above case with that carried out against a constant external pressure p_f .

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ANSWERS

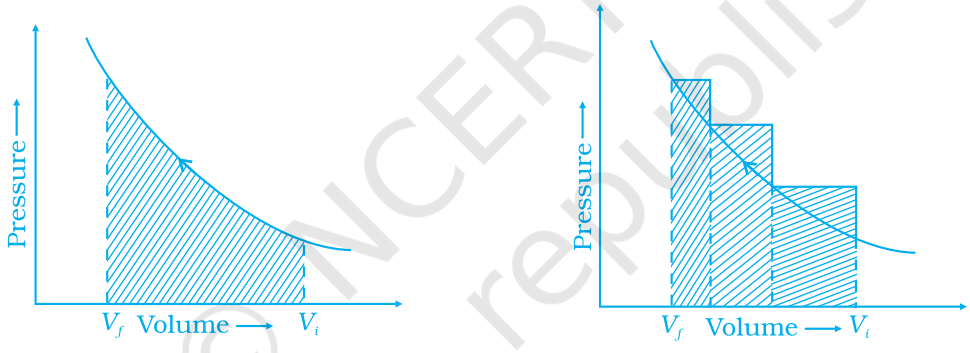
I. Multiple Choice Questions (Type-I)

1. (iii) 2. (iii) 3. (iv) 4. (iii) 5. (iii) 6. (ii)

7. (iii)
Justification : free expansion w = 0
adiabatic process q = 0
ΔU = q + w = 0, this means that internal energy remains constant. Therefore, ΔT = 0.

In ideal gas there is no intermolecular attraction. Hence when such a gas expands under adiabatic conditions into a vaccum no heat is absorbed or evolved since no external work is done to separate the molecules.

8. (ii) w (reversible) < w (irreversible)
Justification : Area under the curve is always more in irreversible compression as can be seen from Fig. 6.5 (a) and (b).



(a) Reversible compression (b) Irreversible compression

Fig. : *6.5*

9. (iii)

Justification : Freezing is exothermic process. The heat released increases the entropy of surrounding.

10. (iii)

11. (iii)

Justification : Same bonds are formed in reaction (a) and (b) but bonds between reactant molecules are broken only in reaction (b).

12. (iii) 13. (i) 14. (ii)

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II. Multiple Choice Questions (Type-II)

15. (i), (iv) 16. (i), (ii) 17. (iii), (iv)

18. (iii), (iv)

Justification : $$\frac{w_{600K}}{w_{300K}} = \frac{1 \times R \times 600\ K \ln \frac{10}{1}}{1 \times R \times 300\ K \ln \frac{10}{1}} = \frac{600}{300} = 2$$

For isothermal expansion of ideal gases, $\Delta U = 0$

since temperature is constant this means there is no change in internal energy. Therefore, $\Delta U = 0$

19. (i), (iii)

III. Short Answer Type

20. + 81.58 kJ, $\Delta_{vap}H^{\ominus}$ = + 40.79 kJ mol^{-1}

21. Water

22. No, since $CaCO_3$ has been formed from other compounds and not from its constituent elements.

23. $\Delta_r H^{\ominus}$ = +91.8 kJ mol^{-1}

24. $\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 .....$

25. $\frac{1665}{4}$ kJ mol^{-1} = 416.2 kJ mol^{-1}

26. +735.5 kJ mol^{-1}

27. It is spontaneous process. Although enthalpy change is zero but randomness or disorder (i.e., ΔS) increases. Therefore, in equation $\Delta G = \Delta H - T\Delta S$, the term $T\Delta S$ will be negative. Hence, ΔG will be negative.

28. $\Delta S = \frac{q_{rev}}{T}$

29. Yes

30. The reaction is spontaneous

$\Delta_r G^{\ominus} = -RT \ln K_p$

31. ΔH (cycle) = 0

32. Less, because ice is more ordered than H_2O (l).

33. State Functions : Enthalpy, Entropy, Temperature, Free energy

Path Functions : Heat, Work

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34. Because of strong hydrogen bonding in water, its enthalpy of vapourisation is more.

35. $\Delta_r G$ will always be zero.

$\Delta_r G^{\ominus}$ is zero for K = 1 because $\Delta G^{\ominus} = -$ RT lnK, $\Delta G^{\ominus}$ will be non zero for other values of K.

36. For isolated system, there is no transfer of energy as heat or as work i.e., w=0 and q=0. According to the first law of thermodynamics.

$$\Delta U = q + w$$
$$= 0 + 0 = 0$$
$$\therefore \quad \Delta U = 0$$

37. **At constant volume**

By first law of thermodynamics:

$$q = \Delta U + (-w)$$
$$(-w) = p\Delta V$$
$$\therefore \quad q = \Delta U + p\Delta V$$
$$\Delta V = 0, \text{ since volume is constant.}$$
$$\therefore \quad q_V = \Delta U + 0$$
$$\Rightarrow \quad q_V = \Delta U = \text{change in internal energy}$$

At constant pressure

$$q_p = \Delta U + p\Delta V$$
$$\text{But, } \Delta U + p\Delta V = \Delta H$$
$$\therefore \quad q_p = \Delta H = \text{change in enthalpy.}$$

So, at a constant volume and at constant pressure heat change is a state function because it is equal to change in internal energy and change in enthalpy respectively which are state functions.

38. $(-w) = p_{ext}(V_2 - V_1) = 0 \times (5 - 1) = 0$

For isothermal expansion $q = 0$

By first law of thermodynamics

$$q = \Delta U + (-w)$$
$$\Rightarrow \quad 0 = \Delta U + 0 \text{ so } \Delta U = 0$$

39. For water, heat capacity = 18 × specific heat

or $C_p = 18 \times c$

Specific heat = c = 4.18 $Jg^{-1}K^{-1}$

Heat capacity = $C_p = 18 \times 4.18\ JK^{-1} = 75.3\ J\ K^{-1}$

40. $C_p - C_V = nR$

$= 10 \times 4.184$ J

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41. Molar enthalpy change of graphite = enthalpy change for 1 g carbon × molar mass of carbon

$= -20.7\ \text{kJ g}^{-1} \times 12\text{g mol}^{-1}$

$\therefore\ \Delta H = -2.48 \times 10^{2}\ \text{kJ mol}^{-1}$

Negative value of $\Delta H \Rightarrow$ exothermic reaction.

42. $\Delta_r H^{\ominus}$ = Bond energy of H_2 + Bond energy of Br_2 – 2 × Bond energy of HBr

$= 435 + 192 - (2 \times 368)\ \text{kJ mol}^{-1}$

$\Rightarrow \Delta_r H^{\ominus} = -109\ \text{kJ mol}^{-1}$

43. $q_p = \Delta H = 30.5\ \text{kJ mol}^{-1}$

$\therefore$ Heat required for vapourisation of 284 g of $CCl_4 = \dfrac{284\text{g}}{154\text{g mol}^{-1}} \times 30.5\ \text{kJ mol}^{-1}$

$= 56.2\ \text{kJ}$

44. According to the definition of standard enthalpy of formation, the enthalpy change for the following reaction will be standard enthalpy of formation of $H_2O\ (l)$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l).$$

or the standard enthalpy of formation of $H_2O(l)$ will be half of the enthalpy of the given equation i.e., $\Delta_r H^{\ominus}$ is also halved.

$$\Delta_f H^{\ominus}_{H_2O}(l) = \frac{1}{2} \times \Delta_r H^{\ominus} = \frac{-572\ \text{kJ mol}^{-1}}{2} = -286\ \text{kJ/mol.}$$

45. Work done on an ideal gas can be calculated from p-V graph shown in Fig. 6.6. Work done is equal to the shaded area ABV_IV_{II}.

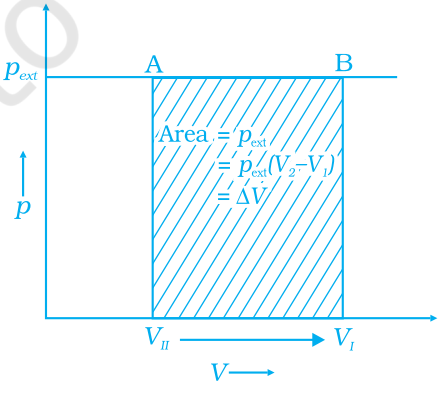

Fig. : *6.6*

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46. The work done can be calculated with the help of p–V plot. A p–V plot of the work of compression which is carried out by change in pressure in infinite steps, is given in Fig. 6.7. Shaded area represents the work done on the gas.

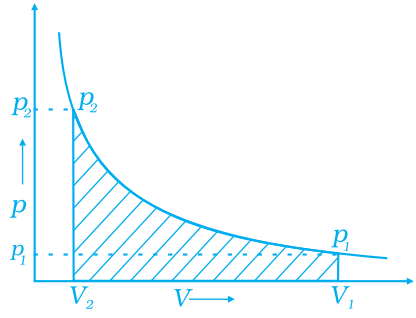

Fig. : *6.7*

47.

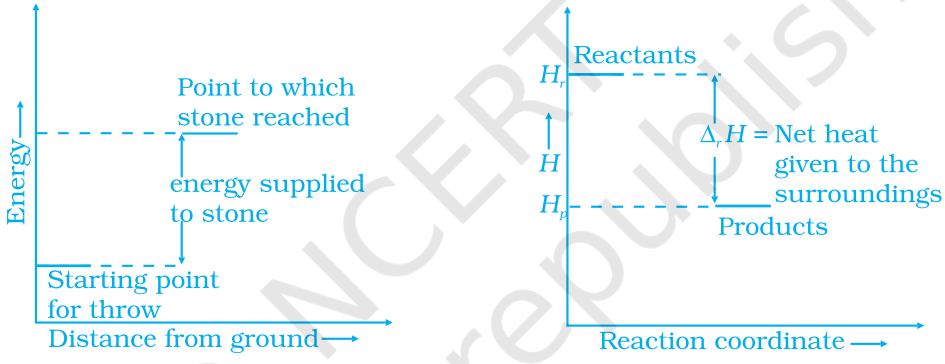

Fig. : *6.8 Enthalpy change in processes (a) and (b)*

48. No.

Enthalpy is one of the contributory factors in deciding spontaneity but it is not the only factor. One must look for contribution of another factor i.e., entropy also, for getting the correct result.

49. It is clear from the figure that the process has been carried out in infinite steps, hence it is isothermal reversible expansion.

$$w = -2.303nRT \log \frac{V_2}{V_1}$$

But, $p_1V_1 = p_2V_2 \quad \Rightarrow \quad \frac{V_2}{V_1} = \frac{p_1}{p_2} = \frac{2}{1} = 2$

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$\therefore \quad w = -2.303\ nRT \log \frac{p_1}{p_2}$

$= -2.303 \times 1\ \text{mol} \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}^{-1} \times \log 2$

$= -2.303 \times 8.314 \times 298 \times 0.3010\ \text{J} = -1717.46\ \text{J}$

50. $w = -p_{ex}(V_f - V_i) = -2 \times 40 = -80\ \text{L bar} = -8\ \text{kJ}$
The negative sign shows that work is done by the system on the surrounding. Work done will be more in the reversible expansion because internal pressure and exernal pressure are almost same at every step.

IV. Matching Type

51. (i) → (e) (ii) → (d) (iii) → (f) (iv) → (a)
(v) → (g), (k), (l) (vi) → (b) (vii) → (c) (viii) → (j)
(ix) → (h) (x) → (i) (xi) → (a), (l), (m) (xii) → (g), (k)

52. (i) →(b) (ii) → (c) (iii) → (a)

53. (i) → (c) (ii) → (a) (iii) → (b)

54. (i) → (b), (d) (ii) → (b) (iii) → (c) (iv) → (a)

V. Assertion and Reason Type

55. (ii) 56. (ii) 57. (i)

VI. Long Answer Type

59. **Hint :** Ratio of two extensive properties is always intensive

$\frac{\text{Extensive}}{\text{Extensive}} = \text{Intensive}$.

e.g., Mole fraction $= \frac{\text{Moles}}{\text{Total number of moles}} = \frac{\text{(Extensive)}}{\text{(Extensive)}}$

60. • $Na(s) + \frac{1}{2}Cl_2(g) \rightarrow Na^+(g) + Cl^-(g)$; $\Delta_{lattice}H^{\ominus}$

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- Bonn - Haber Cycle
- Steps to measure lattice enthalpy from Bonn - Haber cycle
- Sublimation of sodium metal

(1) $Na(s) \rightarrow Na(g)$; $\Delta_{sub}H^{\ominus}$

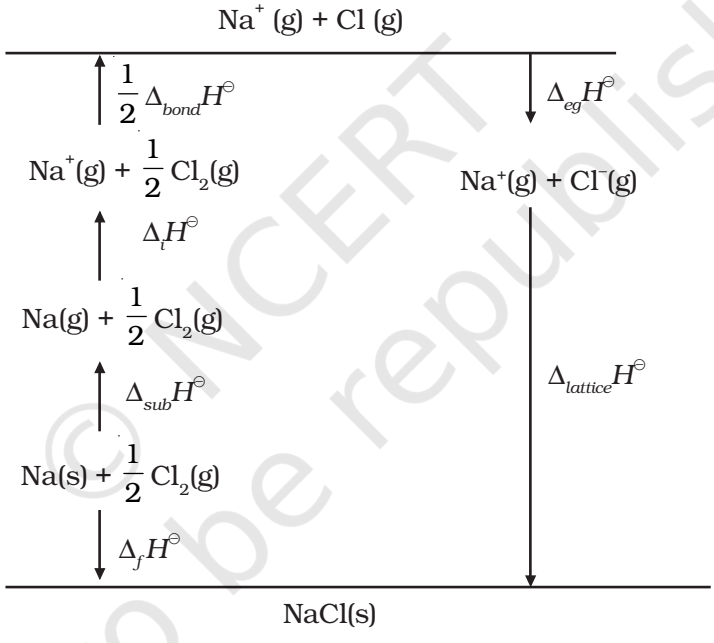
(2) Ionisation of sodium atoms

$Na(g) \rightarrow Na^{+}(g) + e^{-}(g)$; $\Delta_{t}H^{\ominus}$ i.e., ionisation enthalpy

(3) Dissociation of chlorine molecule

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$; $\frac{1}{2}\Delta_{bond}H^{\ominus}$ i.e., One-half of bond dissociation enthalpy.

(4) $Cl(g) + e^{-}(g) \rightarrow Cl^{-}(g)$; $\Delta_{eg}H^{\ominus}$ i.e., electron gain enthalpy.



61. $\Delta S_{Total} = \Delta S_{sys} + \Delta S_{surr}$

$\Delta S_{Total} = \Delta S_{sys} + \frac{-\Delta H_{sys}}{T}$

$T\Delta S_{Total} = T\Delta S_{sys} - \Delta H_{sys}$

For spontaneous change, $\Delta S_{total} > 0$

$\therefore \quad T\Delta S_{sys} - \Delta H_{sys} > 0$

$\Rightarrow \quad -(\Delta H_{sys} - T\Delta S_{sys}) > 0$

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But, $\Delta H_{sys} - T\Delta S_{sys} = \Delta G_{sys}$

$\therefore \quad -\Delta G_{sys} > 0$

$\Rightarrow \quad \Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} < 0$

ΔH_{sys} = Enthalpy change of a reaction.

$T\Delta S_{sys}$ = Energy which is not available to do useful work.

ΔG_{sys} = Energy available for doing useful work.

- Unit of ΔG is Joule
- The reaction will be spontaneous at high temperature.

62.

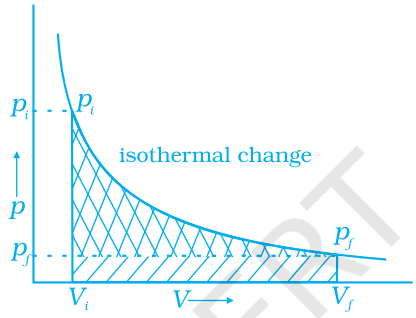

Fig. : *6.9*

(i) Reversible Work is represented by the combined areas and .
(ii) Work against constant pressure, p_f is represented by the area
Work (i) > Work (ii)

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Unit

7

EQUILIBRIUM

I. Multiple Choice Questions (Type-I)

1. We know that the relationship between K_c and K_p is

$K_p = K_c (RT)^{\Delta n}$

What would be the value of Δn for the reaction

$NH_4Cl\ (s) \rightleftharpoons NH_3\ (g) + HCl\ (g)$

(i) 1

(ii) 0.5

(iii) 1.5

(iv) 2

2. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI\ (g)$, the standard free energy is $\Delta G^{\ominus} > 0$. The equilibrium constant (K) would be _____.

(i) $K = 0$

(ii) $K > 1$

(iii) $K = 1$

(iv) $K < 1$

3. Which of the following is **not** a general characteristic of equilibria involving physical processes?

(i) Equilibrium is possible only in a closed system at a given temperature.

(ii) All measurable properties of the system remain constant.

(iii) All the physical processes stop at equilibrium.

(iv) The opposing processes occur at the same rate and there is dynamic but stable condition.

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4. PCl_5, PCl_3 and Cl_2 are at equilibrium at 500K in a closed container and their concentrations are 0.8×10^{-3} mol L^{-1}, 1.2×10^{-3} mol L^{-1} and 1.2×10^{-3} mol L^{-1} respectively. The value of K_c for the reaction $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$ will be

(i) 1.8×10^{3} mol L^{-1}

(ii) 1.8×10^{-3}

(iii) 1.8×10^{-3} L mol^{-1}

(iv) 0.55×10^{4}

5. Which of the following statements is incorrect?

(i) In equilibrium mixture of ice and water kept in perfectly insulated flask mass of ice and water does not change with time.

(ii) The intensity of red colour increases when oxalic acid is added to a solution containing iron (III) nitrate and potassium thiocyanate.

(iii) On addition of catalyst the equilibrium constant value is not affected.

(iv) Equilibrium constant for a reaction with negative ΔH value decreases as the temperature increases.

6. When hydrochloric acid is added to cobalt nitrate solution at room temperature, the following reaction takes place and the reaction mixture becomes blue. On cooling the mixture it becomes pink. On the basis of this information mark the correct answer.

$$\underset{\text{(pink)}}{[Co(H_2O)_6]^{3+}}\ (aq) + 4Cl^-\ (aq) \rightleftharpoons \underset{\text{(blue)}}{[CoCl_4]^{2-}}\ (aq) + 6H_2O\ (l)$$

(i) $\Delta H > 0$ for the reaction

(ii) $\Delta H < 0$ for the reaction

(iii) $\Delta H = 0$ for the reaction

(iv) The sign of ΔH cannot be predicted on the basis of this information.

7. The pH of neutral water at 25°C is 7.0. As the temperature increases, ionisation of water increases, however, the concentration of H^+ ions and OH^- ions are equal. What will be the pH of pure water at 60°C?

(i) Equal to 7.0

(ii) Greater than 7.0

(iii) Less than 7.0

(iv) Equal to zero

8. The ionisation constant of an acid, K_a, is the measure of strength of an acid. The K_a values of acetic acid, hypochlorous acid and formic acid are 1.74×10^{-5}, 3.0×10^{-8} and 1.8×10^{-4} respectively. Which of the following orders of pH of 0.1 mol dm^{-3} solutions of these acids is correct?

(i) acetic acid > hypochlorous acid > formic acid

(ii) hypochlorous acid > acetic acid > formic acid

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(iii) formic acid > hypochlorous acid > acetic acid

(iv) formic acid > acetic acid > hypochlorous acid

9. K_{a_1}, K_{a_2} and K_{a_3} are the respective ionisation constants for the following reactions.

$H_2S \rightleftharpoons H^+ + HS^-$

$HS^- \rightleftharpoons H^+ + S^{2-}$

$H_2S \rightleftharpoons 2H^+ + S^{2-}$

The correct relationship between K_{a_1}, K_{a_2} and K_{a_3} is

(i) $K_{a_3} = K_{a_1} \times K_{a_2}$

(ii) $K_{a_3} = K_{a_1} + K_{a_2}$

(iii) $K_{a_3} = K_{a_1} - K_{a_2}$

(iv) $K_{a_3} = K_{a_1} / K_{a_2}$

10. Acidity of BF_3 can be explained on the basis of which of the following concepts?

(i) Arrhenius concept

(ii) Bronsted Lowry concept

(iii) Lewis concept

(iv) Bronsted Lowry as well as Lewis concept.

11. Which of the following will produce a buffer solution when mixed in equal volumes?

(i) 0.1 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl

(ii) 0.05 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl

(iii) 0.1 mol dm^{-3} NH_4OH and 0.05 mol dm^{-3} HCl

(iv) 0.1 mol dm^{-3} CH_4COONa and 0.1 mol dm^{-3} NaOH

12. In which of the following solvents is silver chloride most soluble?

(i) 0.1 mol dm^{-3} $AgNO_3$ solution

(ii) 0.1 mol dm^{-3} HCl solution

(iii) H_2O

(iv) Aqueous ammonia

13. What will be the value of pH of 0.01 mol dm^{-3} CH_3COOH ($K_a = 1.74 \times 10^{-5}$)?

(i) 3.4

(ii) 3.6

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(iii) 3.9

(iv) 3.0

14. K_a for CH_3COOH is 1.8×10^{-5} and K_b for NH_4OH is 1.8×10^{-5} . The pH of ammonium acetate will be

(i) 7.005

(ii) 4.75

(iii) 7.0

(iv) Between 6 and 7

15. Which of the following options will be correct for the stage of half completion of the reaction $A \rightleftharpoons B$.

(i) $\Delta G^{\ominus} = 0$

(ii) $\Delta G^{\ominus} > 0$

(iii) $\Delta G^{\ominus} < 0$

(iv) $\Delta G^{\ominus} = -RT \ln 2$

16. On increasing the pressure, in which direction will the gas phase reaction proceed to re-establish equilibrium, is predicted by applying the Le Chatelier's principle. Consider the reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Which of the following is correct, if the total pressure at which the equilibrium is established, is increased without changing the temperature?

(i) K will remain same

(ii) K will decrease

(iii) K will increase

(iv) K will increase initially and decrease when pressure is very high

17. What will be the correct order of vapour pressure of water, acetone and ether at 30°C. Given that among these compounds, water has maximum boiling point and ether has minimum boiling point?

(i) Water < ether < acetone

(ii) Water < acetone < ether

(iii) Ether < acetone < water

(iv) Acetone < ether < water

18. At 500 K, equilibrium constant, K_c , for the following reaction is 5.

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

What would be the equilibrium constant K_c for the reaction

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

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(i) 0.04

(ii) 0.4

(iii) 25

(iv) 2.5

19. In which of the following reactions, the equilibrium remains unaffected on addition of small amount of argon at constant volume?

(i) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(ii) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(iii) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(iv) The equilibrium will remain unaffected in all the three cases.

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

20. For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the value of K is 50 at 400 K and 1700 at 500 K. Which of the following options is correct?

(i) The reaction is endothermic

(ii) The reaction is exothermic

(iii) If $NO_2(g)$ and $N_2O_4(g)$ are mixed at 400 K at partial pressures 20 bar and 2 bar respectively, more $N_2O_4(g)$ will be formed.

(iv) The entropy of the system increases.

21. At a particular temperature and atmospheric pressure, the solid and liquid phases of a pure substance can exist in equilibrium. Which of the following term defines this temperature?

(i) Normal melting point

(ii) Equilibrium temperature

(iii) Boiling point

(iv) Freezing point

III. Short Answer Type

22. The ionisation of hydrochloric in water is given below:

$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

Label two conjugate acid-base pairs in this ionisation.

23. The aqueous solution of sugar does not conduct electricity. However, when sodium chloride is added to water, it conducts electricity. How will you explain this statement on the basis of ionisation and how is it affected by concentration of sodium chloride?

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24. BF_3 does not have proton but still acts as an acid and reacts with NH_3. Why is it so? What type of bond is formed between the two?

25. Ionisation constant of a weak base MOH, is given by the expression

$$K_b = \frac{[M^+][OH^-]}{[MOH]}$$

Values of ionisation constant of some weak bases at a particular temperature are given below:

Base	**Dimethylamine**	**Urea**	**Pyridine**	**Ammonia**
K_b	5.4×10^{-4}	1.3×10^{-14}	1.77×10^{-9}	1.77×10^{-5}

Arrange the bases in decreasing order of the extent of their ionisation at equilibrium. Which of the above base is the strongest?

26. Conjugate acid of a weak base is always stronger. What will be the decreasing order of basic strength of the following conjugate bases?

$OH^-, RO^-, CH_3COO^-, Cl^-$

27. Arrange the following in increasing order of pH.

KNO_3 (*aq*), CH_3COONa (*aq*), NH_4Cl (*aq*), $C_6H_5COONH_4$ (*aq*)

28. The value of K_c for the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ is 1×10^{-4}

At a given time, the composition of reaction mixture is

$[HI] = 2 \times 10^{-5}$ mol, $[H_2] = 1 \times 10^{-5}$ mol and $[I_2] = 1 \times 10^{-5}$ mol

In which direction will the reaction proceed?

29. On the basis of the equation $pH = -\log [H^+]$, the pH of 10^{-8} mol dm^{-3} solution of HCl should be 8. However, it is observed to be less than 7.0. Explain the reason.

30. pH of a solution of a strong acid is 5.0. What will be the pH of the solution obtained after diluting the given solution a 100 times?

31. A sparingly soluble salt gets precipitated only when the product of concentration of its ions in the solution (Q_{sp}) becomes greater than its solubility product. If the solubility of $BaSO_4$ in water is 8×10^{-4} mol dm^{-3}. Calculate its solubility in 0.01 mol dm^{-3} of H_2SO_4.

32. pH of 0.08 mol dm^{-3} HOCl solution is 2.85. Calculate its ionisation constant.

33. Calculate the pH of a solution formed by mixing equal volumes of two solutions A and B of a strong acid having pH = 6 and pH = 4 respectively.

34. The solubility product of $Al(OH)_3$ is 2.7×10^{-11}. Calculate its solubility in gL^{-1} and also find out pH of this solution. (Atomic mass of Al = 27 u).

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35. Calculate the volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution. (K_{sp} of $PbCl_2 = 3.2 \times 10^{-8}$, atomic mass of Pb = 207 u).

36. A reaction between ammonia and boron trifluoride is given below:

$: NH_3 + BF_3 \longrightarrow H_3N : BF_3$

Identify the acid and base in this reaction. Which theory explains it? What is the hybridisation of B and N in the reactants?

37. Following data is given for the reaction: $CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$

$\Delta_f H^{\ominus}\,[CaO(s)] = -635.1\ kJ\ mol^{-1}$

$\Delta_f H^{\ominus}\,[CO_2(g)] = -393.5\ kJ\ mol^{-1}$

$\Delta_f H^{\ominus}\,[CaCO_3(s)] = -1206.9\ kJ\ mol^{-1}$

Predict the effect of temperature on the equilibrium constant of the above reaction.

IV. Matching Type

38. Match the following equilibria with the corresponding condition

(i)	Liquid ⇌ Vapour	(a)	Saturated solution
(ii)	Solid ⇌ Liquid	(b)	Boiling point
(iii)	Solid ⇌ Vapour	(c)	Sublimation point
(iv)	Solute (s) ⇌ Solute (solution)	(d)	Melting point
		(e)	Unsaturated solution

39. For the reaction : $N_2\,(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Equilibrium constant $K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

Some reactions are written below in Column I and their equilibrium constants in terms of K_c are written in Column II. Match the following reactions with the corresponding equilibrium constant

	Column I (Reaction)		**Column II (Equilibrium constant)**
(i)	$2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)$	(a)	$2K_c$
(ii)	$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$	(b)	$K_c^{\frac{1}{2}}$
(iii)	$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$	(c)	$\frac{1}{K_c}$
		(d)	K_c^2

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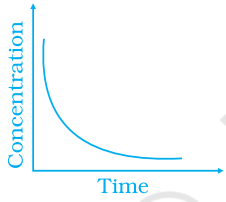
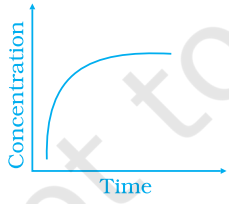
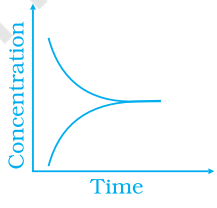
40. Match standard free energy of the reaction with the corresponding equilibrium constant

(i)	$\Delta G^{\ominus} > 0$	(a)	K > 1
(ii)	$\Delta G^{\ominus} < 0$	(b)	K = 1
(iii)	$\Delta G^{\ominus} = 0$	(c)	K = 0
		(d)	K < 1

41. Match the following species with the corresponding conjugate acid

	Species		**Conjugate acid**
(i)	NH_3	(a)	CO_3^{2-}
(ii)	HCO_3^-	(b)	NH_4^+
(iii)	H_2O	(c)	H_3O^+
(iv)	HSO_4^-	(d)	H_2SO_4
		(e)	H_2CO_3

42. Match the following graphical variation with their description

A		**B**
(i)		(a) Variation in product concentration with time
(ii)		(b) Reaction at equilibrium
(iii)		(c) Variation in reactant concentration with time

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43. Match Column (I) with Column (II).

Column I		Column II	
(i)	Equilibrium	(a)	$\Delta G > 0, K < 1$
(ii)	Spontaneous reaction	(b)	$\Delta G = 0$
(iii)	Non spontaneous reaction	(c)	$\Delta G^{\ominus} = 0$
		(d)	$\Delta G < 0, K > 1$

V. Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

44. ***Assertion (A) :*** Increasing order of acidity of hydrogen halides is HF < HCl < HBr < HI

Reason (R) : While comparing acids formed by the elements belonging to the same group of periodic table, H–A bond strength is a more important factor in determining acidity of an acid than the polar nature of the bond.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

45. ***Assertion (A) :*** A solution containing a mixture of acetic acid and sodium acetate maintains a constant value of pH on addition of small amounts of acid or alkali.

Reason (R) : A solution containing a mixture of acetic acid and sodium acetate acts as a buffer solution around pH 4.75.

(i) Both A and R are true and R is correct explanation of A.

(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

46. ***Assertion (A):*** The ionisation of hydrogen sulphide in water is low in the presence of hydrochloric acid.

Reason (R) : Hydrogen sulphide is a weak acid.

(i) Both A and R are true and R is correct explanation of A.

(ii) Both A and R are true but R is not correct explanation of A.

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(iii) A is true but R is false

(iv) Both A and R are false

47. ***Assertion (A):*** For any chemical reaction at a particular temperature, the equilibrium constant is fixed and is a characteristic property.

Reason (R) : Equilibrium constant is independent of temperature.

(i) Both A and R are true and R is correct explanation of A.

(ii) Both A and R are true but R is not correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

48. ***Assertion (A) :*** Aqueous solution of ammonium carbonate is basic.

Reason (R) : Acidic/basic nature of a salt solution of a salt of weak acid and weak base depends on K_a and K_b value of the acid and the base forming it.

(i) Both A and R are true and R is correct explanation of A.

(ii) Both A and R are true but R is not correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

49. ***Assertion (A):*** An aqueous solution of ammonium acetate can act as a buffer.

Reason (R) : Acetic acid is a weak acid and NH_4OH is a weak base.

(i) Both A and R are true and R is correct explanation of A.

(ii) Both A and R are true but R is not correct explanation of A.

(iii) A is false but R is true.

(iv) Both A and R are false.

50. ***Assertion (A):*** In the dissociation of PCl_5 at constant pressure and temperature addition of helium at equilibrium increases the dissociation of PCl_5.

Reason (R) : Helium removes Cl_2 from the field of action.

(i) Both A and R are true and R is correct explanation of A.

(ii) Both A and R are true but R is not correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

VI. Long Answer Type

51. How can you predict the following stages of a reaction by comparing the value of K_c and Q_c?

(i) Net reaction proceeds in the forward direction.

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(ii) Net reaction proceeds in the backward direction.

(iii) No net reaction occurs.

52. On the basis of Le Chatelier principle explain how temperature and pressure can be adjusted to increase the yield of ammonia in the following reaction.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.38 \text{ kJ mol}^{-1}$

What will be the effect of addition of argon to the above reaction mixture at constant volume?

53. A sparingly soluble salt having general formula $A_x^{p+}B_y^{q-}$ and molar solubility S is in equilibrium with its saturated solution. Derive a relationship between the solubility and solubility product for such salt.

54. Write a relation between ΔG and Q and define the meaning of each term and answer the following :

(a) Why a reaction proceeds forward when $Q < K$ and no net reaction occurs when $Q = K$.

(b) Explain the effect of increase in pressure in terms of reaction quotient Q. for the reaction : $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

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ANSWERS

I. Multiple Choice Questions (Type-I)

1. (iv) 2. (iv) 3. (iii) 4. (ii) 5. (ii) 6. (i)

7. (iii) 8. (iv) 9. (i) 10. (iii) 11. (iii) 12. (iv)

13. (i) 14. (iii)

15. (i) $\Delta G^{\ominus} = 0$

Justification : $\Delta G^{\ominus} = -RT \ln K$

At the stage of half completion of reaction [A] = [B], Therefore, $K = 1$.

Thus, $\Delta G^{\ominus} = 0$

16. (i), *Justification*: According to Le-Chatelier's principle, at constant temperature, the equilibrium composition will change but K will remain same.

17. (ii)

18. (i)

19. (iv)

II. Multiple Choice Questions (Type-II)

20. (i), (iii) and (iv)

Justification : (i) K increases with increase in temperature.

(iii) $Q > K$, Therefore, reaction proceeds in the backward direction.

(iv) $\Delta n > 0$, Therefore, $\Delta S > 0$.

21. (i) and (iv)

III. Short Answer Type

22. HCl Cl^-

acid conjugate base

H_2O H_3O^+

base conjugate acid

23. • Sugar does not ionise in water but NaCl ionises completely in water and produces Na^+ and Cl^- ions.

• Conductance increases with increase in concentration of salt due to release of more ions.

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24. BF_3 acts as a Lewis acid as it is electron deficient compound and coordinate bond is formed as given below :

$H_3N : \rightarrow BF_3$

25. • Order of extent of ionisation at equilibrium is as follows :

Dimethylamine > Ammonia > Pyridine > Urea

• Since dimethylamine will ionise to the maximum extent it is the strongest base out of the four given bases.

26. $RO^- > OH^- > CH_3COO^- > Cl^-$

27. $NH_4Cl < C_6H_5COONH_4 < KNO_3 < CH_3COONa$

28. At a given time the reaction quotient Q for the reaction will be given by the expression.

$$Q = \frac{[H_2][I_2]}{[HI]^2}$$

$$= \frac{1\times10^{-5}\times1\times10^{-5}}{(2\times10^{-5})^2} = \frac{1}{4}$$

$= 0.25 = 2.5 \times 10^{-1}$

As the value of reaction quotient is greater than the value of K_c i.e. 1×10^{-4} the reaction will proceed in the reverse direction.

29. Concentration of 10^{-8} mol dm^{-3} indicates that the solution is very dilute. Hence, the contribution of H_3O^+ concentration from water is significant and should also be included for the calculation of pH.

30. (i) pH = 5

$[H^+] = 10^{-5}$ mol L^{-1}

On 100 times dilution

$[H^+] = 10^{-7}$ mol L^{-1}

On calculating the pH using the equation pH = – log $[H^+]$, value of pH comes out to be 7. It is not possible. This indicates that solution is very dilute. Hence,

Total hydrogen ion concentration = $[H^+]$

= [Contribution of H_3O^+ ion concentration of acid] + [Contribution of H_3O^+ ion concentration of water]

= $10^{-7} + 10^{-7}$.

pH = 2×10^{-7} = $7 - \log 2$ = $7 - 0.3010 = 6.6990$

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31.

	$BaSO_4$ (s)	$\rightleftharpoons$	Ba^{2+} (*aq*)	+	SO_4^{2-} (*aq*)
At t = 0	1		0		0
At equilibrium in water	1–S		S		S
At equilibrium in the presence of sulphuric acid	1–S		S		(S+0.01)

K_{sp} for $BaSO_4$ in water = $[Ba^{2+}]\,[SO_4^{2-}]$ = (S) (S) = S^2

But S = 8×10^{-4} mol dm^{-3}

$\therefore\ K_{sp} = (8\times10^{-4})^2 = 64 \times 10^{-8}$ ... (1)

The expression for K_{sp} in the presence of sulphuric acid will be as follows :

K_{sp} = (S) (S + 0.01) ... (2)

Since value of K_{sp} will not change in the presence of sulphuric acid, therefore from (1) and (2)

(S) (S + 0.01) = 64×10^{-8}

$S^2 + 0.01\ S = 64 \times 10^{-8}$

$S^2 + 0.01\ S - 64 \times 10^{-8} = 0$

$$S = \frac{-0.01 \pm \sqrt{(0.01)^2 + (4\times64\times10^{-8})}}{2}$$

$$= \frac{-0.01 \pm \sqrt{10^{-4} + (256\times10^{-8})}}{2}$$

$$= \frac{-0.01 \pm \sqrt{10^{-4}(1 + 256\times10^{-2})}}{2}$$

$$= \frac{-0.01 \pm 10^{-2}\sqrt{1+0.256}}{2}$$

$$= \frac{-0.01 \pm 10^{-2}\sqrt{1.256}}{2}$$

$$= \frac{-10^{-2} + (1.12\times10^{-2})}{2}$$

$$= \frac{(-1+1.12)\times10^{-2}}{2} = \frac{0.12}{2}\times10^{-2}$$

$= 6 \times 10^{-4}$ mol dm^{-3}

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32. pH of HOCl = 2.85

But, – pH = log $[H^+]$

$\therefore$ – 2.85 = log $[H^+]$

$\bar{3}.15$ = log $[H^+]$

$[H^+] = 1.413 \times 10^{-3}$

For weak mono basic acid $[H^+] = \sqrt{K_a \times C}$

$$K_a = \frac{[H^+]^2}{C} = \frac{(1.413 \times 10^{-3})^2}{0.08}$$

$$= 24.957 \times 10^{-6} = 2.4957 \times 10^{-5}$$

33. pH of Solution A = 6

Therefore, concentration of $[H^+]$ ion in solution A = 10^{-6} mol L^{-1}

pH of Solution B = 4

Therefore, Concentration of $[H^+]$ ion concentration of solution B = 10^{-4} mol L^{-1}

On mixing one litre of each solution, total volume = 1L + 1L = 2L

Amount of H^+ ions in 1L of Solution A= Concentration × volume V

= 10^{-6} mol × 1L

Amount of H^+ ions in 1L of solution B = 10^{-4} mol × 1L

$\therefore$ Total amount of H^+ ions in the solution formed by mixing solutions A and B is (10^{-6} mol + 10^{-4} mol)

This amount is present in 2L solution.

$$\therefore \text{ Total } [H^+] = \frac{10^{-4}(1+0.01)}{2} = \frac{1.01 \times 10^{-4}}{2} \text{ mol } L^{-1} = \frac{1.01 \times 10^{-4}}{2} \text{ mol } L^{-1}$$

$$= 0.5 \times 10^{-4} \text{ mol } L^{-1}$$

$$= 5 \times 10^{-5} \text{ mol } L^{-1}$$

pH = – log $[H^+]$ = – log (5×10^{-5})

= – [log 5 + (– 5 log 10)]

= – log 5 + 5

= 5 – log 5

= 5 – 0.6990

= 4.3010 = 4.3

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34. Let S be the solubility of $Al(OH)_3$.

	$Al(OH)_3$	$\rightleftharpoons$	Al^{3+} (aq)	+	$3OH^-$ (aq)
Concentration of species at t = 0	1		0		0
Concentration of various species at equilibrium	1–S		S		3S

$K_{sp} = [Al^{3+}] [OH^-]^3 = (S) (3S)^3 = 27 S^4$

$$S^4 = \frac{K_{sp}}{27} = \frac{27 \times 10^{-11}}{27 \times 10} = 1 \times 10^{-12}$$

$S = 1 \times 10^{-3}$ mol L^{-1}

(i) **Solubility of $Al(OH)_3$**

Molar mass of $Al(OH)_3$ is 78 g. Therefore,

Solubility of $Al(OH)_3$ in g L^{-1} = $1 \times 10^{-3} \times 78$ g L^{-1} = 78×10^{-3} g L^{-1}

= 7.8×10^{-2} g L^{-1}

(ii) **pH of the solution**

$S = 1 \times 10^{-3}$ mol L^{-1}

$[OH^-] = 3S = 3 \times 1 \times 10^{-3} = 3 \times 10^{-3}$

pOH = 3 – log 3

pH = 14 – pOH = 11 + log 3 = 11.4771

35. K_{sp} of $PbCl_2 = 3.2 \times 10^{-8}$

Let S be the solubility of $PbCl_2$.

	$PbCl_2$ (s)	$\rightleftharpoons$	Pb^{2+} (aq)	+	$2Cl^-$ (aq)
Concentration of species at t = 0	1		0		0
Concentration of various species at equilibrium	1–S		S		2S

$K_{sp} = [Pb^{2+}] [Cl^-]^2 = (S) (2S)^2 = 4S^3$

$K_{sp} = 4S^3$

$$S^3 = \frac{K_{sp}}{4} = \frac{3.2 \times 10^{-8}}{4} \text{ mol } L^{-1} = 8 \times 10^{-9} \text{ mol } L^{-1}$$

$S = \sqrt[3]{8 \times 10^{-9}} = 2 \times 10^{-3}$ mol L^{-1} $\therefore$ $S = 2 \times 10^{-3}$ mol L^{-1}

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Molar mass of $PbCl_2$ = 278

$\therefore$ Solubility of $PbCl_2$ in g L^{-1} = $2 \times 10^{-3} \times 278$ g L^{-1}

= 556×10^{-3} g L^{-1}

= 0.556 g L^{-1}

To get saturated solution, 0.556 g of $PbCl_2$ is dissolved in 1 L water.

0.1 g $PbCl_2$ is dissolved in $\frac{0.1}{0.556}$ L = 0.1798 L water.

To make a saturated solution, dissolution of 0.1 g $PbCl_2$ in 0.1798 L $\approx$ 0.2 L of water will be required.

37. $\Delta_r H^{\ominus} = \Delta_f H^{\ominus}$ [CaO(s)] + $\Delta_f H^{\ominus}$ [CO_2(g)] – $\Delta_f H^{\ominus}$ [$CaCO_3$(s)]

$\therefore$ $\Delta_r H^{\ominus}$ = 178.3 kJ mol^{-1}

The reaction is endothermic. Hence, according to Le-Chatelier's principle, reaction will proceed in forward direction on increasing temperature.

IV. Matching Type

38. (i) → (b) (ii) → (d) (iii) → (c) (iv) → (a)

39. (i) → (d) (ii) → (c) (iii) → (b)

40. (i) → (d) (ii) → (a) (iii) → (b)

41. (i) → (b) (ii) → (e) (iii) → (c) (iv) → (d)

42. (i) → (c) (ii) → (a) (iii) → (b)

43. (i) → (b) and (c) (ii) → (d) (iii) → (a)

V. Assertion and Reason Type

44. (i) 45. (i) 46. (ii) 47.(iii) 48. (i) 49. (iii)

50. (iv)

VI. Long Answer Type

51. (i) $Q_c < K_c$

(ii) $Q_c > K_c$

(iii) $Q_c = K_c$

where, Q_c is reaction quotient in terms of concentration and K_c is equilibrium constant.

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53. [**Hint :** $A_x^{p+}B_y^{q-} \rightleftharpoons x\,A^{p+}(aq) + y\,B^{q-}(aq)$

S moles of A_xB_y dissolve to give x S moles of A^{p+} and y S moles of B^{q-}.]

54. $\Delta G = \Delta G^{\ominus} + RT\ln Q$

$\Delta G^{\ominus}$ = Change in free energy as the reaction proceeds

ΔG = Standard free energy change

Q = Reaction quotient

R = Gas constant

T = Absolute temperature

Since $\Delta G^{\ominus} = -RT\ln K$

$$\therefore \quad \Delta G = -RT\ln K + RT\ln Q = RT\ln\frac{Q}{K}$$

If $Q < K$, ΔG will be negative. Reaction proceeds in the forward direction.

If $Q = K$, $\Delta G = 0$, no net reaction.

[**Hint:** Next relate Q with concentration of CO, H_2, CH_4 and H_2O in view of reduced volume (increased pressure). Show that $Q < K$ and hence the reaction proceeds in forward direction.]

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Unit

8

REDOX REACTIONS

I. Multiple Choice Questions (Type-I)

1. Which of the following is **not** an example of redox reaction?

(i) $CuO + H_2 \longrightarrow Cu + H_2O$

(ii) $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$

(iii) $2K + F_2 \longrightarrow 2KF$

(iv) $BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$

2. The more positive the value of $E^{\ominus}$, the greater is the tendency of the species to get reduced. Using the standard electrode potential of redox couples given below find out which of the following is the strongest oxidising agent.

$E^{\ominus}$ values: $Fe^{3+}/Fe^{2+} = + 0.77$; $I_2(s)/I^- = + 0.54$;

$Cu^{2+}/Cu = + 0.34$; $Ag^+/Ag = + 0.80V$

(i) Fe^{3+}

(ii) $I_2(s)$

(iii) Cu^{2+}

(iv) Ag^+

3. $E^{\ominus}$ values of some redox couples are given below. On the basis of these values choose the correct option.

$E^{\ominus}$ values : $Br_2/Br^- = + 1.90$; $Ag^+/Ag(s) = + 0.80$

$Cu^{2+}/Cu(s) = + 0.34$; $I_2(s)/I^- = + 0.54$

(i) Cu will reduce Br^-

(ii) Cu will reduce Ag

(iii) Cu will reduce I^-

(iv) Cu will reduce Br_2

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4. Using the standard electrode potential, find out the pair between which redox reaction is **not** feasible.

$E^{\ominus}$ values : $Fe^{3+}/Fe^{2+} = + 0.77$; $I_2/I^- = + 0.54$;

$Cu^{2+}/Cu = + 0.34$; $Ag^+/Ag = + 0.80$ V

(i) Fe^{3+} and I^-

(ii) Ag^+ and Cu

(iii) Fe^{3+} and Cu

(iv) Ag and Fe^{3+}

5. Thiosulphate reacts differently with iodine and bromine in the reactions given below:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

$$S_2O_3^{2-} + 2Br_2 + 5H_2O \rightarrow 2SO_4^{2-} + 2Br^- + 10\ H^+$$

Which of the following statements justifies the above dual behaviour of thiosulphate?

(i) Bromine is a stronger oxidant than iodine.

(ii) Bromine is a weaker oxidant than iodine.

(iii) Thiosulphate undergoes oxidation by bromine and reduction by iodine in these reactions.

(iv) Bromine undergoes oxidation and iodine undergoes reduction in these reactions.

6. The oxidation number of an element in a compound is evaluated on the basis of certain rules. Which of the following rules is **not** correct in this respect?

(i) The oxidation number of hydrogen is always +1.

(ii) The algebraic sum of all the oxidation numbers in a compound is zero.

(iii) An element in the free or the uncombined state bears oxidation number zero.

(iv) In all its compounds, the oxidation number of fluorine is – 1.

7. In which of the following compounds, an element exhibits two different oxidation states.

(i) NH_2OH

(ii) NH_4NO_3

(iii) N_2H_4

(iv) N_3H

8. Which of the following arrangements represent increasing oxidation number of the central atom?

(i) CrO_2^- , ClO_3^- , CrO_4^{2-} , MnO_4^-

(ii) ClO_3^- , CrO_4^{2-} , MnO_4^- , CrO_2^-

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(iii) CrO_2^- , ClO_3^- , MnO_4^- , CrO_4^{2-}

(iv) CrO_4^{2-}, MnO_4^- , CrO_2^- , ClO_3^-

9. The largest oxidation number exhibited by an element depends on its outer electronic configuration. With which of the following outer electronic configurations the element will exhibit largest oxidation number?

(i) $3d^1 4s^2$

(ii) $3d^3 4s^2$

(iii) $3d^5 4s^1$

(iv) $3d^5 4s^2$

10. Identify disproportionation reaction

(i) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

(ii) $CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4HCl$

(iii) $2F_2 + 2OH^- \longrightarrow 2F^- + OF_2 + H_2O$

(iv) $2NO_2 + 2OH^- \longrightarrow NO_2^- + NO_3^- + H_2O$

11. Which of the following elements does **not** show disproportionation tendency?

(i) Cl

(ii) Br

(iii) F

(iv) I

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

12. Which of the following statement(s) is/are **not** true about the following decomposition reaction.

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

(i) Potassium is undergoing oxidation

(ii) Chlorine is undergoing oxidation

(iii) Oxygen is reduced

(iv) None of the species are undergoing oxidation or reduction

13. Identify the correct statement (s) in relation to the following reaction:

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

(i) Zinc is acting as an oxidant

(ii) Chlorine is acting as a reductant

(iii) Hydrogen ion is acting as an oxidant

(iv) Zinc is acting as a reductant

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14. The exhibition of various oxidation states by an element is also related to the outer orbital electronic configuration of its atom. Atom(s) having which of the following outermost electronic configurations will exhibit more than one oxidation state in its compounds.

(i) $3s^1$

(ii) $3d^1 4s^2$

(iii) $3d^2 4s^2$

(iv) $3s^2 3p^3$

15. Identify the correct statements with reference to the given reaction

$$P_4 + 3OH^- + 3H_2O \rightarrow PH_3 + 3H_2PO_2^-$$

(i) Phosphorus is undergoing reduction only.

(ii) Phosphorus is undergoing oxidation only.

(iii) Phosphorus is undergoing oxidation as well as reduction.

(iv) Hydrogen is undergoing neither oxidation nor reduction.

16. Which of the following electrodes will act as anodes, when connected to Standard Hydrogen Electrode?

(i)	Al/Al^{3+}	$E^{\ominus} = -1.66$
(ii)	Fe/Fe^{2+}	$E^{\ominus} = -0.44$
(iii)	Cu/Cu^{2+}	$E^{\ominus} = +0.34$
(iv)	$F_2(g)/2F^-(aq)$	$E^{\ominus} = +2.87$

III. Short Answer Type

17. The reaction

$$Cl_2(g) + 2OH^-(aq) \longrightarrow ClO^-(aq) + Cl^-(aq) + H_2O(l)$$

represents the process of bleaching. Identify and name the species that bleaches the substances due to its oxidising action.

18. MnO_4^{2-} undergoes disproportionation reaction in acidic medium but MnO_4^- does not. Give reason.

19. PbO and PbO_2 react with HCl according to following chemical equations :

$$2PbO + 4HCl \longrightarrow 2PbCl_2 + 2H_2O$$

$$PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$$

Why do these compounds differ in their reactivity?

20. Nitric acid is an oxidising agent and reacts with PbO but it does not react with PbO_2. Explain why?

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21. Write balanced chemical equation for the following reactions:

(i) Permanganate ion (MnO_4^-) reacts with sulphur dioxide gas in acidic medium to produce Mn^{2+} and hydrogensulphate ion.

(Balance by ion electron method)

(ii) Reaction of liquid hydrazine (N_2H_4) with chlorate ion (ClO_3^-) in basic medium produces nitric oxide gas and chloride ion in gaseous state.

(Balance by oxidation number method)

(iii) Dichlorine heptaoxide (Cl_2O_7) in gaseous state combines with an aqueous solution of hydrogen peroxide in acidic medium to give chlorite ion (ClO_2^-) and oxygen gas.

(Balance by ion electron method)

22. Calculate the oxidation number of phosphorus in the following species.

(a) HPO_3^{2-} and (b) PO_4^{3-}

23. Calculate the oxidation number of each sulphur atom in the following compounds:

(a) $Na_2S_2O_3$ (b) $Na_2S_4O_6$ (c) Na_2SO_3 (d) Na_2SO_4

24. Balance the following equations by the oxidation number method.

(i) $Fe^{2+} + H^+ + Cr_2O_7^{2-} \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

(ii) $I_2 + NO_3^- \longrightarrow NO_2 + IO_3^-$

(iii) $I_2 + S_2O_3^{2-} \longrightarrow I^- + S_4O_6^{2-}$

(iv) $MnO_2 + C_2O_4^{2-} \longrightarrow Mn^{2+} + CO_2$

25. Identify the redox reactions out of the following reactions and identify the oxidising and reducing agents in them.

(i) $3HCl(aq) + HNO_3\,(aq) \longrightarrow Cl_2\,(g) + NOCl\,(g) + 2H_2O\,(l)$

(ii) $HgCl_2\,(aq) + 2KI\,(aq) \longrightarrow HgI_2\,(s) + 2KCl\,(aq)$

(iii) $Fe_2O_3\,(s) + 3CO\,(g) \xrightarrow{\Delta} 2Fe\,(s) + 3CO_2\,(g)$

(iv) $PCl_3\,(l) + 3H_2O\,(l) \longrightarrow 3HCl\,(aq) + H_3PO_3\,(aq)$

(v) $4NH_3 + 3O_2\,(g) \longrightarrow 2N_2\,(g) + 6H_2O\,(g)$

26. Balance the following ionic equations

(i) $Cr_2O_7^{2-} + H^+ + I^- \longrightarrow Cr^{3+} + I_2 + H_2O$

(ii) $Cr_2O_7^{2-} + Fe^{2+} + H^+ \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

(iii) $MnO_4^- + SO_3^{2-} + H^+ \longrightarrow Mn^{2+} + SO_4^{2-} + H_2O$

(iv) $MnO_4^- + H^+ + Br^- \longrightarrow Mn^{2+} + Br_2 + H_2O$

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IV. Matching Type

27. Match Column I with Column II for the oxidation states of the central atoms.

	Column I	**Column II**
(i)	$Cr_2O_7^{2-}$	(a) + 3
(ii)	MnO_4^-	(b) + 4
(iii)	VO_3^-	(c) + 5
(iv)	FeF_6^{3-}	(d) + 6
		(e) + 7

28. Match the items in Column I with relevant items in Column II.

	Column I	**Column II**
(i)	Ions having positive charge	(a) +7
(ii)	The sum of oxidation number of all atoms in a neutral molecule	(b) –1
		(c) +1
(iii)	Oxidation number of hydrogen ion (H^+)	(d) 0
(iv)	Oxidation number of fluorine in NaF	(e) Cation
(v)	Ions having negative charge	(f) Anion

V. Assertion and Reason Type

In the following questions a statement of assertion (A) followed by a statement of reason (R) is given. Choose the correct option out of the choices given below each question.

29. ***Assertion (A) :*** Among halogens fluorine is the best oxidant.

Reason (R) : Fluorine is the most electronegative atom.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

30. ***Assertion (A):*** In the reaction between potassium permanganate and potassium iodide, permanganate ions act as oxidising agent.

Reason (R) : Oxidation state of manganese changes from +2 to +7 during the reaction.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

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31. ***Assertion (A) :*** The decomposition of hydrogen peroxide to form water and oxygen is an example of disproportionation reaction.

Reason (R) : The oxygen of peroxide is in –1 oxidation state and it is converted to zero oxidation state in O_2 and –2 oxidation state in H_2O.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

32. ***Assertion (A) :*** Redox couple is the combination of oxidised and reduced form of a substance involved in an oxidation or reduction half cell.

Reason (R) : In the representation $E^{\ominus}_{Fe^{3+}/Fe^{2+}}$ and $E^{\ominus}_{Cu^{2+}/Cu}$, Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu are redox couples.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

VI. Long Answer Type

33. Explain redox reactions on the basis of electron transfer. Give suitable examples.

34. On the basis of standard electrode potential values, suggest which of the following reactions would take place? (Consult the book for $E^{\ominus}$ value).

(i) $Cu + Zn^{2+} \longrightarrow Cu^{2+} + Zn$

(ii) $Mg + Fe^{2+} \longrightarrow Mg^{2+} + Fe$

(iii) $Br_2 + 2Cl^- \longrightarrow Cl_2 + 2Br^-$

(iv) $Fe + Cd^{2+} \longrightarrow Cd + Fe^{2+}$

35. Why does fluorine not show disporportionation reaction?

36. Write redox couples involved in the reactions (i) to (iv) given in question 34.

37. Find out the oxidation number of chlorine in the following compounds and arrange them in increasing order of oxidation number of chlorine.

$NaClO_4$, $NaClO_3$, NaClO, $KClO_2$, Cl_2O_7, ClO_3, Cl_2O, NaCl, Cl_2, ClO_2.

Which oxidation state is not present in any of the above compounds?

38. Which method can be used to find out strength of reductant/oxidant in a solution? Explain with an example.

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ANSWERS

I. Multiple Choice Questions (Type-I)

1. (iv) 2. (iv) 3. (iv) 4. (iv) 5. (i) 6. (i)
7. (ii) 8. (i) 9. (iv) 10. (iv) 11. (iii)

II. Multiple Choice Questions (Type-II)

12. (i), (iv) 13. (iii), (iv) 14. (iii), (iv)
15. (iii), (iv) 16. (i), (ii)

III. Short Answer Type

17. Hypochlorite ion

18. In MnO_4^-, Mn is in the highest oxidation state i.e. +7. Therefore, it does not undergo disproportionation. MnO_4^{2-} undergoes disproportionation as follows :

$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

19. $2PbO + 4HCl \longrightarrow 2PbCl_2 + 2H_2O$ (Acid base reaction)

$PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$ (Redox reaction)

(***Hint :*** Note the oxidation number of lead in the oxides)

20. PbO is a basic oxide and simple acid base reaction takes place between PbO and HNO_3. On the other hand in PbO_2 lead is in + 4 oxidation state and cannot be oxidised further. Therefore no reaction takes place. Thus, PbO_2 is passive, only PbO reacts with HNO_3.

$2PbO + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + 2H_2O$ (Acid base reaction)

22. (a) +3, (b) +5

23. (a) +2 (b) +5, 0, 0, +5 (c) +4 (d) +6

Justification :

Write Lewis structure of each ion then assign electron pair shared between atoms of different electronegativity to more electronegative atom and distribute the electron pair shared between atoms of same element equally. Now count the number of electrons possessed by each atom. Find out the difference in number of electrons possessed by neutral atom and that possessed by atom in the compound. This difference is the oxidation number. If atom present in the compound possesses more electrons than the neutral atom, the oxidation

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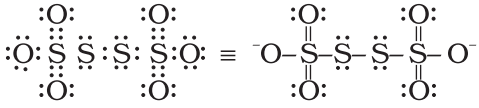
number is negative. If it possesses less electrons then oxidation number is positive.

(i) Lewis structure of $S_2O_4^{2-}$ can be written as follows :

Electron pair shared between sulphur and oxygen atom is assigned to oxygen atom because of more electronegativity of oxygen. Thus each sulphur atom is deficient of two electrons with respect to neutral sulphur atom. Hence, each sulphur atom is in +2 oxidation state. Each oxygen atom gets two excess electrons hence it is in –2 oxidation state. Lewis structure of $S_4O_6^{2-}$ can be written as follows :



To find out oxidation state of each atom we distribute electrons of electron pair shared between two sulphur atoms equally (i.e. one electron is assigned to each sulphur atom). Both electrons of electron pair shared between sulphur and oxygen atom are assigned to oxygen as oxygen is more electronegative. Thus we find that each of the central sulphur atoms obtains six electrons. This number is same as that in the outer shell of neutral sulphur atom. Hence, oxidation state of each central sulphur atom is zero. Each of the sulphur atoms attached to oxygen atoms finally obtains only one electron as its share. This number is less by five electrons in comparison to the neutral sulphur atom. So, outer sulphur atoms are in +5 oxidation state. Therefore average oxidation state of sulphur atoms is :

$$\frac{5+0+0+5}{4} = \frac{10}{4} = 2.5$$

By using the formula we obtain average oxidation state of the particular type of atoms. Real oxidation state can be obtained only by writing the complete structural formula. Similarly we can see that each oxygen atom is in – 2 oxidation state.

In the same way one can find out the oxidation state of each atom in SO_3^{2-} and SO_4^{2-} ions. Oxidation state of metal atoms will be +1 as these will lose one electron in each case.

IV. Matching Type

27. (i)→ (d) (ii)→ (e) (iii) → (c) (iv)→(a)

28. (i)→ (e) (ii) → (d) (iii) → (c) (iv) → (b) (v) → (f)

V. Assertion and Reason Type

29. (ii) 30. (iii) 31. (i) 32. (ii)

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Unit

9

HYDROGEN

I. Multiple Choice Questions (Type-I)

1. Hydrogen resembles halogens in many respects for which several factors are responsible. Of the following factors which one is most important in this respect?

(i) Its tendency to lose an electron to form a cation.

(ii) Its tendency to gain a single electron in its valence shell to attain stable electronic configuration.

(iii) Its low negative electron gain enthalpy value.

(iv) Its small size.

2. Why does H^+ ion always get associated with other atoms or molecules?

(i) Ionisation enthalpy of hydrogen resembles that of alkali metals.

(ii) Its reactivity is similar to halogens.

(iii) It resembles both alkali metals and halogens.

(iv) Loss of an electron from hydrogen atom results in a nucleus of very small size as compared to other atoms or ions. Due to smal size it cannot exist free.

3. Metal hydrides are ionic, covalent or molecular in nature. Among LiH, NaH, KH, RbH, CsH, the correct order of increasing ionic character is

(i) LiH > NaH > CsH > KH>RbH

(ii) LiH < NaH < KH < RbH < CsH

(iii) RbH > CsH > NaH > KH > LiH

(iv) NaH > CsH > RbH > LiH > KH

4. Which of the following hydrides is electron-precise hydride?

(i) B_2H_6

(ii) NH_3

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(iii) H_2O

(iv) CH_4

5. Radioactive elements emit α, β and γ rays and are characterised by their half-lives. The radioactive isotope of hydrogen is

(i) Protium

(ii) Deuterium

(iii) Tritium

(iv) Hydronium

6. Consider the reactions

(A) $H_2O_2 + 2HI \longrightarrow I_2 + 2H_2O$ (B) $HOCl + H_2O_2 \longrightarrow H_3O^+ + Cl^- + O_2$

Which of the following statements is correct about H_2O_2 with reference to these reactions? Hydrogen perioxide is _____.

(i) an oxidising agent in both (A) and (B)

(ii) an oxidising agent in (A) and reducing agent in (B)

(iii) a reducing agent in (A) and oxidising agent in (B)

(iv) a reducing agent in both (A) and (B)

7. The oxide that gives H_2O_2 on treatment with dilute H_2SO_4 is —

(i) PbO_2

(ii) $BaO_2.8H_2O + O_2$

(iii) MnO_2

(iv) TiO_2

8. Which of the following equations depict the oxidising nature of H_2O_2?

(i) $2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

(ii) $2Fe^{3+} + 2H^+ + H_2O_2 \longrightarrow 2Fe^{2+} + 2H_2O + O_2$

(iii) $2I^- + 2H^+ + H_2O_2 \longrightarrow I_2 + 2H_2O$

(iv) $KIO_4 + H_2O_2 \longrightarrow KIO_3 + H_2O + O_2$

9. Which of the following equation depicts reducing nature of H_2O_2?

(i) $2[Fe(CN)_6]^{4-} + 2H^+ + H_2O_2 \longrightarrow 2[Fe(CN)_6]^{3-} + 2H_2O$

(ii) $I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$

(iii) $Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$

(iv) $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$

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10. Hydrogen peroxide is _____.

(i) an oxidising agent

(ii) a reducing agent

(iii) both an oxidising and a reducing agent

(iv) neither oxidising nor reducing agent

11. Which of the following reactions increases production of dihydrogen from synthesis gas?

(i) $CH_4(g) + H_2O(g) \xrightarrow[Ni]{1270\,K} CO(g) + 3H_2(g)$

(ii) $C(s) + H_2O(g) \xrightarrow{1270\,K} CO(g) + H_2(g)$

(iii) $CO(g) + H_2O(g) \xrightarrow[Catalyst]{673\,K} CO_2(g) + H_2(g)$

(iv) $C_2H_6 + 2H_2O \xrightarrow[Ni]{1270\,K} 2CO + 5H_2$

12. When sodium peroxide is treated with dilute sulphuric acid, we get _____.

(i) sodium sulphate and water

(ii) sodium sulphate and oxygen

(iii) sodium sulphate, hydrogen and oxygen

(iv) sodium sulphate and hydrogen peroxide

13. Hydrogen peroxide is obtained by the electrolysis of _____.

(i) water

(ii) sulphuric acid

(iii) hydrochloric acid

(iv) fused sodium peroxide

14. Which of the following reactions is an example of use of water gas in the synthesis of other compounds?

(i) $CH_4(g) + H_2O(g) \xrightarrow[Ni]{1270\,K} CO(g) + H_2(g)$

(ii) $CO(g) + H_2O(g) \xrightarrow[Catalyst]{673\,K} CO_2(g) + H_2(g)$

(iii) $C_nH_{2n+2} + nH_2O(g) \xrightarrow[Ni]{1270\,K} nCO + (2n+1)\,H_2$

(iv) $CO(g) + 2H_2(g) \xrightarrow[Catalyst]{Cobalt} CH_3OH(l)$

15. Which of the following ions will cause hardness in water sample?

(i) Ca^{2+}

(ii) Na^{+}

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(iii) Cl^-

(iv) K^+

16. Which of the following compounds is used for water softening?

(i) $Ca_3(PO_4)_2$

(ii) Na_3PO_4

(iii) $Na_6P_6O_{18}$

(iv) Na_2HPO_4

17. Elements of which of the following group(s) of periodic table do **not** form hydrides.

(i) Groups 7, 8, 9

(ii) Group 13

(iii) Groups 15, 16, 17

(iv) Group 14

18. Only one element of _____ forms hydride.

(i) group 6

(ii) group 7

(iii) group 8

(iv) group 9

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

19. Which of the following statements are **not** true for hydrogen?

(i) It exists as diatomic molecule.

(ii) It has one electron in the outermost shell.

(iii) It can lose an electron to form a cation which can freely exist

(iv) It forms a large number of ionic compounds by losing an electron.

20. Dihydrogen can be prepared on commercial scale by different methods. In its preparation by the action of steam on hydrocarbons, a mixture of CO and H_2 gas is formed. It is known as _____.

(i) Water gas

(ii) Syngas

(iii) Producer gas

(d) Industrial gas

21. Which of the following statement(s) is/are correct in the case of heavy water?

(i) Heavy water is used as a moderator in nuclear reactor.

(ii) Heavy water is more effective as solvent than ordinary water.

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(iii) Heavy water is more associated than ordinary water.
(iv) Heavy water has lower boiling point than ordinary water.

22. Which of the following statements about hydrogen are correct?
(i) Hydrogen has three isotopes of which protium is the most common.
(ii) Hydrogen never acts as cation in ionic salts.
(iii) Hydrogen ion, H^+, exists freely in solution.
(iv) Dihydrogen does not act as a reducing agent.

23. Some of the properties of water are described below. Which of them is/are **not** correct?
(i) Water is known to be a universal solvent.
(ii) Hydrogen bonding is present to a large extent in liquid water.
(iii) There is no hydrogen bonding in the frozen state of water.
(iv) Frozen water is heavier than liquid water.

24. Hardness of water may be temporary or permanent. Permanent hardness is due to the presence of
(i) Chlorides of Ca and Mg in water
(ii) Sulphates of Ca and Mg in water
(iii) Hydrogen carbonates of Ca and Mg in water
(iv) Carbonates of alkali metals in water

25. Which of the following statements is correct?
(i) Elements of group 15 form electron deficient hydrides.
(ii) All elements of group 14 form electron precise hydrides.
(iii) Electron precise hydrides have tetrahedral geometries.
(iv) Electron rich hydrides can act as Lewis acids.

26. Which of the following statements is correct?
(i) Hydrides of group 13 act as Lewis acids.
(ii) Hydrides of group 14 are electron deficient hydrides.
(iii) Hydrides of group 14 act as Lewis acids.
(iv) Hydrides of group 15 act as Lewis bases.

27. Which of the following statements is correct?
(i) Metallic hydrides are deficient of hydrogen.
(ii) Metallic hydrides conduct heat and electricity.
(iii) Ionic hydrides do not conduct electricity in solid state.
(iv) Ionic hydrides are very good conductors of electricity in solid state.

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III. Short Answer Type

28. How can production of hydrogen from water gas be increased by using water gas shift reaction?

29. What are metallic/interstitial hydrides? How do they differ from molecular hydrides?

30. Name the classes of hydrides to which H_2O, B_2H_6 and NaH belong.

31. If same mass of liquid water and a piece of ice is taken, then why is the density of ice less than that of liquid water?

32. Complete the following equations:

(i) $PbS\ (s) + H_2O_2(aq) \longrightarrow$ (ii) $CO\ (g) + 2H_2\ (g) \xrightarrow[Catalyst]{Cobalt}$

33. Give reasons:

(i) Lakes freeze from top towards bottom.

(ii) Ice floats on water.

34. What do you understand by the term 'auto protolysis of water' ? What is its significance?

35. Discuss briefly de-mineralisation of water by ion exchange resin.

36. Molecular hydrides are classified as electron deficient, electron precise and electron rich compounds. Explain each type with two examples.

37. How is heavy water prepared? Compare its physical properties with those of ordinary water.

38. Write one chemical reaction for the preparation of D_2O_2.

39. Calculate the strength of 5 volume H_2O_2 solution.

40. (i) Draw the gas phase and solid phase structure of H_2O_2.

(ii) H_2O_2 is a better oxidising agent than water. Explain.

41. Melting point, enthalpy of vapourisation and viscosity data of H_2O and D_2O is given below :

	H_2O	**D_2O**
Melting point / K	373.0	374.4
Enthalpy of vapourisation at (373 K)/ kJ mol^{-1}	40.66	41.61
Viscosity/centipoise	0.8903	1.107

On the basis of this data explain in which of these liquids intermolecular forces are stronger?

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42. Dihydrogen reacts with dioxygen (O_2) to form water. Write the name and formula of the product when the isotope of hydrogen which has one proton and one neutron in its nucleus is treated with oxygen. Will the reactivity of both the isotopes be the same towards oxygen? Justify your answer.

43. Explain why HCl is a gas and HF is a liquid.

44. When the first element of the periodic table is treated with dioxygen, it gives a compound whose solid state floats on its liquid state. This compound has an ability to act as an acid as well as a base. What products will be formed when this compound undergoes autoionisation?

45. Rohan heard that instructions were given to the laboratory attendent to store a particular chemical i.e., keep it in the dark room, add some urea in it, and keep it away from dust. This chemical acts as an oxidising as well as a reducing agent in both acidic and alkaline media. This chemical is important for use in the pollution control treatment of domestic and industrial effluents.

(i) Write the name of this compound.

(ii) Explain why such precautions are taken for storing this chemical.

46. Give reasons why hydrogen resembles alkali metals?

47. Hydrogen generally forms covalent compounds. Give reason.

48. Why is the Ionisation enthalpy of hydrogen higher than that of sodium?

49. Basic principle of hydrogen economy is transportation and storage of energy in the form of liquid or gaseous hydrogen. Which property of hydrogen may be useful for this purpose? Support your answer with the chemical equation if required.

50. What is the importance of heavy water?

51. Write the Lewis structure of hydrogen peroxide.

52. An acidic solution of hydrogen peroxide behaves as an oxidising as well as reducing agent. Illustrate it with the help of a chemical equation.

53. With the help of suitable examples, explain the property of H_2O_2 that is responsible for its bleaching action?

54. Why is water molecule polar?

55. Why does water show high boiling point as compared to hydrogen sulphide? Give reasons for your answer.

56. Why can dilute solutions of hydrogen peroxide not be concentrated by heating. How can a concentrated solution of hydrogen peroxide be obtained?

57. Why is hydrogen peroxide stored in wax lined bottles?

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58. Why does hard water not form lather with soap?

59. Phosphoric acid is preferred over sulphuric acid in preparing hydrogen peroxide from peroxides. Why?

60. How will you account for 104.5° bond angle in water?

61. Write redox reaction between fluorine and water.

62. Write two reactions to explain amphoteric nature of water.

IV. Matching Type

63. Correlate the items listed in Column I with those listed in Column II. Find out as many correlations as you can.

Column I	**Column II**
(i) Synthesis gas	(a) $Na_2[Na_4(PO_3)_6]$
(ii) Dihydrogen	(b) Oxidising agent
(iii) Heavy water	(c) Softening of water
(iv) Calgon	(d) Reducing agent
(v) Hydrogen peroxide	(e) Stoichiometric compounds of s-block elements
(vi) Salt like hydrides	(f) Prolonged electrolysis of water
	(g) Zn + NaOH
	(h) Zn + dil. H_2SO_4
	(i) Synthesis of methanol
	(j) Mixture of CO and H_2

64. Match Column I with Column II for the given properties/applications mentioned therein.

Column I	**Column II**
(i) H	(a) Used in the name of perhydrol.
(ii) H_2	(b) Can be reduced to dihydrogen by NaH.
(iii) H_2O	(c) Can be used in hydroformylation of olefin.
(iv) H_2O_2	(d) Can be used in cutting and welding.

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65. Match the terms in Column I with the relevant item in Column II.

	Column I		**Column II**
(i)	Electrolysis of water produces	(a)	atomic reactor
(ii)	Lithium aluminium hydride is used as	(b)	polar molecule
(iii)	Hydrogen chloride is a	(c)	recombines on metal surface to generate high temperature
(iv)	Heavy water is used in	(d)	reducing agent
(v)	Atomic hydrogen	(e)	hydrogen and oxygen

66. Match the items in Column I with the relevant item in Column II.

	Column I		**Column II**
(i)	Hydrogen peroxide is used as a	(a)	zeolite
(ii)	Used in Calgon method	(b)	perhydrol
(iii)	Permanent hardness of hard water is removed by	(c)	sodium hexametaphosphate
		(d)	propellant

V. Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the options given below each question.

67. ***Assertion (A) :*** Permanent hardness of water is removed by treatment with washing soda.

Reason (R) : Washing soda reacts with soluble magnesium and calcium sulphate to form insoluble carbonates.

(i) Statements A and R both are correct and R is the correct explanation of A.

(ii) A is correct but R is not correct.

(iii) A and R both are correct but R is not the correct explanation of A.

(iv) A and R both are false.

68. ***Assertion (A) :*** Some metals like platinum and palladium, can be used as storage media for hydrogen.

Reason (R) : Platinum and palladium can absorb large volumes of hydrogen.

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(i) Statements A and R both are correct and R is the correct explanation of A.

(ii) A is correct but R is not correct.

(iii) A and R both are correct but R is not the correct explanation of A.

(iv) A and R both are false.

VI. Long Answer Type

69. Atomic hydrogen combines with almost all elements but molecular hydrogen does not. Explain.

70. How can D_2O be prepared from water? Mention the physical properties in which D_2O differs from H_2O. Give at least three reactions of D_2O showing the exchange of hydrogen with deuterium.

71. How will you concentrate H_2O_2? Show differences between structures of H_2O_2 and H_2O by drawing their spatial structures. Also mention three important uses of H_2O_2.

72. (i) Give a method for the manufacture of hydrogen peroxide and explain the reactions involved therein.

(ii) Illustrate oxidising, reducing and acidic properties of hydrogen peroxide with equations.

73. What mass of hydrogen peroxide will be present in 2 litres of a 5 molar solution? Calculate the mass of oxygen which will be liberated by the decomposition of 200 mL of this solution.

74. A colourless liquid 'A' contains H and O elements only. It decomposes slowly on exposure to light. It is stabilised by mixing urea to store in the presence of light.

(i) Suggest possible structure of A.

(ii) Write chemical equations for its decomposition reaction in light.

75. An ionic hydride of an alkali metal has significant covalent character and is almost unreactive towards oxygen and chlorine. This is used in the synthesis of other useful hydrides. Write the formula of this hydride. Write its reaction with Al_2Cl_6.

76. Sodium forms a crystalline ionic solid with dihydrogen. The solid is non-volatile and non- conducting in nature. It reacts violently with water to produce dihydrogen gas. Write the formula of this compound and its reaction with water. What will happen on electrolysis of the melt of this solid.

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ANSWERS

I. Multiple Choice Questions (Type-I)

1. (ii)	2. (iv)	3. (ii)	4. (iv)	5. (iii)	6. (ii)
7. (ii)	8. (iii)	9. (ii)	10. (iii)	11. (iii)	12. (iv)
13. (ii)	14. (iv)	15. (i)	16. (iii)	17. (i)	18. (i)

II. Multiple Choice Questions (Type-II)

19. (iii), (iv)	20. (i), (ii)	21. (i), (iii)
22. (i), (ii)	23. (iii), (iv)	24. (i), (ii)
25. (ii), (iii)	26. (i), (iv)	27. (i), (ii), (iii)

III. Short Answer Type

39. 5 volume H_2O_2 solution means that hydrogen peroxide contained in 1 volume of this solution will decompose to give 5 volumes of oxygen at STP i.e. if 1L of this solution is taken, then 5 L of oxygen can be produced from this at STP. Chemical equation for the decomposition of H_2O_2 is $2H_2O_2(l) \longrightarrow O_2(g) + H_2O(l)$.

It shows that 68 g H_2O_2 gives 22.7 L of O_2 at STP, so 5 L oxygen will be obtained from :

$$\frac{68g \times 5L}{22.7L} = \frac{3400}{227} g\ H_2O_2 = 14.9\ g \approx 15\ g\ H_2O_2$$

i.e., 15 g H_2O_2 dissolved in 1 L solution will give 5 L oxygen or 1.5 g H_2O_2/100 mL solution will give 500 mL oxygen. Thus 15 g/L or 1.5% solution is known as 5V solution of H_2O_2.

42. [***Hint :*** Heavy water; Bond dissociation energy of dihydrogen is less than dideuterium]

44. [***Hint :*** $H_2O + H_2O \longrightarrow H_3O^+ + {}^-OH$]

45. (i) H_2O_2

IV. Matching Type

63. (i) → (i), (j) (ii) → (d), (e), (g), (h), (i)

(iii) → (f) (iv) → (a), (c)

(v) → (b), (d) (vi) → (e)

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64. (i) → (d) (ii) → (c) (iii) → (b) (iv) → (a)

65. (i) → (e) (ii) → (d) (iii) → (b) (iv) → (a)
(v) → (c)

66. (i) → (b), (d) (ii) → (c) (iii) → (a), (c)

V. Assertion and Reason Type

67. (i) 68. (i)

VI. Long Answer Type

73. 68 g, 3.2 g

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Unit

10

THE s -BLOCK ELEMENTS

I. Multiple Choice Questions (Type-I)

1. The alkali metals are low melting. Which of the following alkali metal is expected to melt if the room temperature rises to 30°C?

(i) Na
(ii) K
(iii) Rb
(iv) Cs

2. Alkali metals react with water vigorously to form hydroxides and dihydrogen. Which of the following alkali metals reacts with water least vigorously?

(i) Li
(ii) Na
(iii) K
(iv) Cs

3. The reducing power of a metal depends on various factors. Suggest the factor which makes Li, the strongest reducing agent in aqueous solution.

(i) Sublimation enthalpy
(ii) Ionisation enthalpy
(iii) Hydration enthalpy
(iv) Electron-gain enthalpy

4. Metal carbonates decompose on heating to give metal oxide and carbon dioxide. Which of the metal carbonates is most stable thermally?

(i) $MgCO_3$
(ii) $CaCO_3$
(iii) $SrCO_3$
(iv) $BaCO_3$

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5. Which of the carbonates given below is unstable in air and is kept in CO_2 atmosphere to avoid decomposition.

(i) $BeCO_3$

(ii) $MgCO_3$

(iii) $CaCO_3$

(iv) $BaCO_3$

6. Metals form basic hydroxides. Which of the following metal hydroxide is the least basic?

(i) $Mg(OH)_2$

(ii) $Ca(OH)_2$

(iii) $Sr(OH)_2$

(iv) $Ba(OH)_2$

7. Some of the Group 2 metal halides are covalent and soluble in organic solvents. Among the following metal halides, the one which is soluble in ethanol is

(i) $BeCl_2$

(ii) $MgCl_2$

(iii) $CaCl_2$

(iv) $SrCl_2$

8. The order of decreasing ionisation enthalpy in alkali metals is

(i) Na > Li > K > Rb

(ii) Rb < Na < K < Li

(iii) Li > Na > K > Rb

(iv) K < Li < Na < Rb

9. The solubility of metal halides depends on their nature, lattice enthalpy and hydration enthalpy of the individual ions. Amongst fluorides of alkali metals, the lowest solubility of LiF in water is due to

(i) Ionic nature of lithium fluoride

(ii) High lattice enthalpy

(iii) High hydration enthalpy for lithium ion.

(iv) Low ionisation enthalpy of lithium atom

10. Amphoteric hydroxides react with both alkalies and acids. Which of the following Group 2 metal hydroxides is soluble in sodium hydroxide?

(i) $Be(OH)_2$

(ii) $Mg(OH)_2$

(iii) $Ca(OH)_2$

(iv) $Ba(OH)_2$

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11. In the synthesis of sodium carbonate, the recovery of ammonia is done by treating NH_4Cl with $Ca(OH)_2$. The by-product obtained in this process is

(i) $CaCl_2$

(ii) NaCl

(iii) NaOH

(iv) $NaHCO_3$

12. When sodium is dissolved in liquid ammonia, a solution of deep blue colour is obtained. The colour of the solution is due to

(i) ammoniated electron

(ii) sodium ion

(iii) sodium amide

(iv) ammoniated sodium ion

13. By adding gypsum to cement

(i) setting time of cement becomes less.

(ii) setting time of cement increases.

(iii) colour of cement becomes light.

(iv) shining surface is obtained.

14. Dead burnt plaster is

(i) $CaSO_4$

(ii) $CaSO_4 . \frac{1}{2} H_2O$

(iii) $CaSO_4.H_2O$

(iv) $CaSO_4.2H_2O$

15. Suspension of slaked lime in water is known as

(i) lime water

(ii) quick lime

(iii) milk of lime

(iv) aqueous solution of slaked lime

16. Which of the following elements does not form hydride by direct heating with dihydrogen?

(i) Be

(ii) Mg

(iii) Sr

(iv) Ba

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17. The formula of soda ash is

(i) $Na_2CO_3.10H_2O$

(ii) $Na_2CO_3.2H_2O$

(iii) $Na_2CO_3.H_2O$

(iv) Na_2CO_3

18. A substance which gives brick red flame and breaks down on heating to give oxygen and a brown gas is

(i) Magnesium nitrate

(ii) Calcium nitrate

(iii) Barium nitrate

(iv) Strontium nitrate

19. Which of the following statements is true about $Ca(OH)_2$?

(i) It is used in the preparation of bleaching powder

(ii) It is a light blue solid

(iii) It does not possess disinfectant property.

(iv) It is used in the manufacture of cement.

20. A chemical **A** is used for the preparation of washing soda to recover ammonia. When CO_2 is bubbled through an aqueous solution of **A**, the solution turns milky. It is used in white washing due to disinfectant nature. What is the chemical formula of **A**?

(i) $Ca(HCO_3)_2$

(ii) CaO

(iii) $Ca(OH)_2$

(iv) $CaCO_3$

21. Dehydration of hydrates of halides of calcium, barium and strontium i.e., $CaCl_26H_2O$, $BaCl_2.2H_2O$, $SrCl_2.2H_2O$, can be achieved by heating. These become wet on keeping in air. Which of the following statements is correct about these halides?

(i) act as dehydrating agent

(ii) can absorb moisture from air

(iii) Tendency to form hydrate decreases from calcium to barium

(iv) All of the above

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

22. Metallic elements are described by their standard electrode potential, fusion enthalpy, atomic size, etc. The alkali metals are characterised by which of the following properties?

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(i) High boiling point
(ii) High negative standard electrode potential
(iii) High density
(iv) Large atomic size

23. Several sodium compounds find use in industries. Which of the following compounds are used for textile industry?
(i) Na_2CO_3
(ii) $NaHCO_3$
(iii) NaOH
(iv) NaCl

24. Which of the following compounds are readily soluble in water?
(i) $BeSO_4$
(ii) $MgSO_4$
(iii) $BaSO_4$
(iv) $SrSO_4$

25. When Zeolite, which is hydrated sodium aluminium silicate is treated with hard water, the sodium ions are exchanged with which of the following ion(s)?
(i) H^+ ions
(ii) Mg^{2+} ions
(iii) Ca^{2+} ions
(iv) SO_4^{2-} ions

26. Identify the correct formula of halides of alkaline earth metals from the following.
(i) $BaCl_2.2H_2O$
(ii) $BaCl_2.4H_2O$
(iii) $CaCl_2.6H_2O$
(iv) $SrCl_2.4H_2O$

27. Choose the correct statements from the following.
(i) Beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.
(ii) Beryllium sulphate is readily soluble in water as the greater hydration enthalpy of Be^{2+} overcomes the lattice enthalpy factor.
(iii) Beryllium exhibits coordination number more than four.
(iv) Beryllium oxide is purely acidic in nature.

28. Which of the following are the correct reasons for anomalous behaviour of lithium?
(i) Exceptionally small size of its atom
(ii) Its high polarising power
(iii) It has high degree of hydration
(iv) Exceptionally low ionisation enthalpy

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III. Short Answer Type

29. How do you account for the strong reducing power of lithium in aqueous solution?

30. When heated in air, the alkali metals form various oxides. Mention the oxides formed by Li, Na and K.

31. Complete the following reactions

(i) $O_2^{2-} + H_2O \longrightarrow$ (ii) $O_2^{-} + H_2O \longrightarrow$

32. Lithium resembles magnesium in some of its properties. Mention two such properties and give reasons for this resemblance.

33. Name an element from Group 2 which forms an amphoteric oxide and a water soluble sulphate.

34. Discuss the trend of the following:

(i) Thermal stability of carbonates of Group 2 elements.

(ii) The solubility and the nature of oxides of Group 2 elements.

35. Why are $BeSO_4$ and $MgSO_4$ readily soluble in water while $CaSO_4$, $SrSO_4$ and $BaSO_4$ are insoluble?

36. All compounds of alkali metals are easily soluble in water but lithium compounds are more soluble in organic solvents. Explain.

37. In the Solvay process, can we obtain sodium carbonate directly by treating the solution containing $(NH_4)_2CO_3$ with sodium chloride? Explain.

38. Write Lewis strucure of O_2^- ion and find out oxidation state of each oxygen atom? What is the average oxidation state of oxygen in this ion?

39. Why do beryllium and magnesium not impart colour to the flame in the flame test?

40. What is the structure of $BeCl_2$ molecule in gaseous and solid state?

IV. Matching Type

In the following questions more than one option of column I and II may be correlated.

41. Match the elements given in Column I with the properties mentioned in Column II.

Column I	**Column II**
(i) Li	(a) Insoluble sulphate
(ii) Na	(b) Strongest monoacidic base
(iii) Ca	(c) Most negative $E^{\ominus}$ value among alkali metals.
(iv) Ba	(d) Insoluble oxalate
	(e) $6s^2$ outer electronic configuration

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42. Match the compounds given in Column I with their uses mentioned in Column II.

Column I		Column II	
(i)	$CaCO_3$	(a)	Dentistry, ornamental work
(ii)	$Ca(OH)_2$	(b)	Manufacture of sodium carbonate from caustic soda
(iii)	CaO	(c)	Manufacture of high quality paper
(iv)	$CaSO_4$	(d)	Used in white washing

43. Match the elements given in Column I with the colour they impart to the flame given in Column II.

Column I		Column II	
(i)	Cs	(a)	Apple green
(ii)	Na	(b)	Violet
(iii)	K	(c)	Brick red
(iv)	Ca	(d)	Yellow
(v)	Sr	(e)	Crimson red
(vi)	Ba	(f)	Blue

V. Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

44. ***Assertion (A):*** The carbonate of lithium decomposes easily on heating to form lithium oxide and CO_2.

Reason (R) : Lithium being very small in size polarises large carbonate ion leading to the formation of more stable Li_2O and CO_2.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct

(iv) A is not correct but R is correct.

45. ***Assertion (A):*** Beryllium carbonate is kept in the atmosphere of carbon dioxide.

Reason (R) : Beryllium carbonate is unstable and decomposes to give beryllium oxide and carbon dioxide.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

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VI. Long Answer Type

46. The *s*-block elements are characterised by their larger atomic sizes, lower ionisation enthalpies, invariable +1 oxidation state and solubilities of their oxosalts. In the light of these features describe the nature of their oxides, halides and oxosalts.

47. Present a comparative account of the alkali and alkaline earth metals with respect to the following characteristics:

(i) Tendency to form ionic / covalent compounds

(ii) Nature of oxides and their solubility in water

(iii) Formation of oxosalts

(iv) Solubility of oxosalts

(v) Thermal stability of oxosalts

48. When a metal of group 1 was dissolved in liquid ammonia, the following observations were obtained:

(i) Blue solution was obtained initially.

(ii) On concentrating the solution, blue colour changed to bronze colour.

How do you account for the blue colour of the solution? Give the name of the product formed on keeping the solution for some time.

49. The stability of peroxide and superoxide of alkali metals increase as we go down the group. Explain giving reason.

50. When water is added to compound (A) of calcium, solution of compound (B) is formed. When carbon dioxide is passed into the solution, it turns milky due to the formation of compound (C). If excess of carbon dioxide is passed into the solution milkiness disappears due to the formation of compound (D). Identify the compounds A, B, C and D. Explain why the milkiness disappears in the last step.

51. Lithium hydride can be used to prepare other useful hydrides. Beryllium hydride is one of them. Suggest a route for the preparation of beryllium hydride starting from lithium hydride. Write chemical equations involved in the process.

52. An element of group 2 forms covalent oxide which is amphoteric in nature and dissolves in water to give an amphoteric hydroxide. Identify the element and write chemical reactions of the hydroxide of the element with an alkali and an acid.

53. Ions of an element of group 1 participate in the transmission of nerve signals and transport of sugars and aminoacids into cells. This element imparts yellow colour to the flame in flame test and forms an oxide and a peroxide with oxygen. Identify the element and write chemical reaction to show the formation of its peroxide. Why does the element impart colour to the flame?

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ANSWERS

I. Multiple Choice Questions (Type-I)

1. (iv)	2. (i)	3. (iii)	4. (iv)	5. (i)	6. (i)
7. (i)	8. (iii)	9. (ii)	10. (i)	11. (i)	12. (i)
13. (ii)	14. (i)	15. (iii)	16. (i)	17. (iv)	18. (ii)
19. (i)	20. (iii)	21. (iv)			

II. Multiple Choice Questions (Type-II)

22. (ii), (iv)	23. (i), (iii)	24. (i), (ii)	25. (ii), (iii)
26. (i), (iii)	27. (i), (ii)	28. (i), (ii)	

III. Short Answer Type

31. (i) $O_2^{2-} + 2H_2O \longrightarrow 2OH^- + H_2O_2$

(ii) $2O_2^- + 2H_2O \longrightarrow 2OH^- + H_2O_2 + O_2$

IV. Matching Type

41.	(i)→ (c),	(ii)→ (b),	(iii)→(d),	(iv)→(a), (e)
42.	(i)→ (c),	(ii) → (d),	(iii) → (b),	(iv) → (a)
43.	(i)→ (f),	(ii) → (d),	(iii) → (b),	(iv) → (c)
	(v)→ (e),	(vi) → (a)		

V. Assertion and Reason Type

44. (i) 45. (i)

VI. Long Answer Type

50. Compound : A : CaO; B : Ca $(OH)_2$; C : $CaCO_3$; D : $Ca(HCO_3)_2$

$Ca(HCO_3)_2$ is soluble in water. Hence, milkiness of solution disappears on passing excess carbon dioxide into the solution of compound B.

51. $8\ LiH + Al_2Cl_6 \longrightarrow 2Li\ Al\ H_4 + 6\ LiCl$

$LiAl\ H_4 + 2BeCl_2 \longrightarrow 2BeH_2 + LiCl + AlCl_3$

52. The element is beryllium

53. The element is sodium.

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Unit

11

THE *p* -BLOCK ELEMENTS

I. Multiple Choice Questions (Type-I)

1. The element which exists in liquid state for a wide range of temperature and can be used for measuring high temperature is

(i) B
(ii) Al
(iii) Ga
(iv) In

2. Which of the following is a Lewis acid ?

(i) $AlCl_3$
(ii) $MgCl_2$
(iii) $CaCl_2$
(iv) $BaCl_2$

3. The geometry of a complex species can be understood from the knowledge of type of hybridisation of orbitals of central atom. The hybridisation of orbitals of central atom in $[Be(OH)_4]^-$ and the geometry of the complex are respectively

(i) sp^3, tetrahedral
(ii) sp^3, square planar
(iii) sp^3d^2, octahedral
(iv) dsp^2, square planar

4. Which of the following oxides is acidic in nature?

(i) B_2O_3
(ii) Al_2O_3
(iii) Ga_2O_3
(iv) In_2O_3

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5. The exhibition of highest co-ordination number depends on the availability of vacant orbitals in the central atom. Which of the following elements is **not** likely to act as central atom in MF_6^{3-}?

(i) B

(ii) Al

(iii) Ga

(iv) In

6. Boric acid is an acid because its molecule

(i) contains replaceable H^+ ion

(ii) gives up a proton

(iii) accepts OH^- from water releasing proton

(iv) combines with proton from water molecule

7. Catenation i.e., linking of similar atoms depends on size and electronic configuration of atoms. The tendency of catenation in Group 14 elements follows the order:

(i) C > Si > Ge > Sn

(ii) C >> Si > Ge ≈ Sn

(iii) Si > C > Sn > Ge

(iv) Ge > Sn > Si > C

8. Silicon has a strong tendency to form polymers like silicones. The chain length of silicone polymer can be controlled by adding

(i) $MeSiCl_3$

(ii) Me_2SiCl_2

(iii) Me_3SiCl

(iv) Me_4Si

9. Ionisation enthalpy ($\Delta_i H_1$ kJ mol^{-1}) for the elements of Group 13 follows the order.

(i) B > Al > Ga > In > Tl

(ii) B < Al < Ga < In < Tl

(iii) B < Al > Ga < In > Tl

(iv) B > Al < Ga > In < Tl

10. In the structure of diborane

(i) All hydrogen atoms lie in one plane and boron atoms lie in a plane perpendicular to this plane.

(ii) 2 boron atoms and 4 terminal hydrogen atoms lie in the same plane and 2 bridging hydrogen atoms lie in the perpendicular plane.

(iii) 4 bridging hydrogen atoms and boron atoms lie in one plane and two terminal hydrogen atoms lie in a plane perpendicular to this plane.

(iv) All the atoms are in the same plane.

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11. A compound X, of boron reacts with NH_3 on heating to give another compound Y which is called inorganic benzene. The compound X can be prepared by treating BF_3 with Lithium aluminium hydride. The compounds X and Y are represented by the formulas.

(i) B_2H_6, $B_3N_3H_6$

(ii) B_2O_3, $B_3N_3H_6$

(iii) BF_3, $B_3N_3H_6$

(iv) $B_3N_3H_6$, B_2H_6

12. Quartz is extensively used as a piezoelectric material, it contains _____.

(i) Pb

(ii) Si

(iii) Ti

(iv) Sn

13. The most commonly used reducing agent is

(i) $AlCl_3$

(ii) $PbCl_2$

(iii) $SnCl_4$

(iv) $SnCl_2$

14. Dry ice is

(i) Solid NH_3

(ii) Solid SO_2

(iii) Solid CO_2

(iv) Solid N_2

15. Cement, the important building material is a mixture of oxides of several elements. Besides calcium, iron and sulphur, oxides of elements of which of the group (s) are present in the mixture?

(i) group 2

(ii) groups 2, 13 and 14

(iii) groups 2 and 13

(iv) groups 2 and 14

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

16. The reason for small radius of Ga compared to Al is _____.

(i) poor screening effect of *d* and *f* orbitals

(ii) increase in nuclear charge

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(iii) presence of higher orbitals

(iv) higher atomic number

17. The linear shape of CO_2 is due to _____.

(i) sp^3 hybridisation of carbon

(ii) sp hybridisation of carbon

(iii) $p\pi - p\pi$ bonding between carbon and oxygen

(iv) sp^2 hybridisation of carbon

18. Me_3SiCl is used during polymerisation of organo silicones because

(i) the chain length of organo silicone polymers can be controlled by adding Me_3SiCl

(ii) Me_3SiCl blocks the end terminal of silicone polymer

(iii) Me_3SiCl improves the quality and yield of the polymer

(iv) Me_3SiCl acts as a catalyst during polymerisation

19. Which of the following statements are correct?

(i) Fullerenes have dangling bonds

(ii) Fullerenes are cage-like molecules

(iii) Graphite is thermodynamically most stable allotrope of carbon

(iv) Graphite is slippery and hard and therefore used as a dry lubricant in machines

20. Which of the following statements are correct. Answer on the basis of Fig. 11.1.

(i) The two birdged hydrogen atoms and the two boron atoms lie in one plane;

(ii) Out of six B–H bonds two bonds can be described in terms of 3 centre 2-electron bonds.

(iii) Out of six B-H bonds four B-H bonds can be described in terms of 3 centre 2 electron bonds;

(iv) The four terminal B-H bonds are two centre-two electron regular bonds.

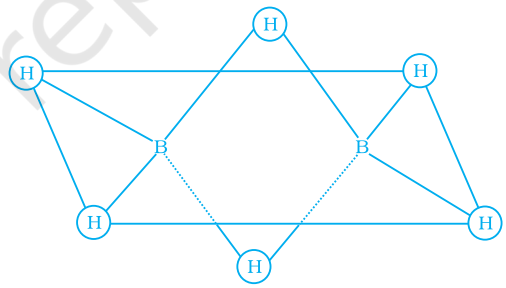

Fig. *11.1*

21. Identify the correct resonance structures of carbon dioxide from the ones given below :

(i) $O - C \equiv O$

(ii) $O = C = O$

(iii) $^{-}O \equiv C - O^{+}$

(iv) $^{-}O - C \equiv O^{+}$

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III. Short Answer Type

22. Draw the structures of $BCl_3.NH_3$ and $AlCl_3$ (dimer).

23. Explain the nature of boric acid as a Lewis acid in water.

24. Draw the structure of boric acid showing hydrogen bonding. Which species is present in water? What is the hybridisation of boron in this species?

25. Explain why the following compounds behave as Lewis acids?

(i) BCl_3 (ii) $AlCl_3$

26. Give reasons for the following:

(i) CCl_4 is immiscible in water, whereas $SiCl_4$ is easily hydrolysed.

(ii) Carbon has a strong tendency for catenation compared to silicon.

27. Explain the following :

(i) CO_2 is a gas whereas SiO_2 is a solid.

(ii) Silicon forms SiF_6^{2-} ion whereas corresponding fluoro compound of carbon is not known.

28. The +1 oxidation state in group 13 and +2 oxidation state in group 14 becomes more and more stable with increasing atomic number. Explain.

29. Carbon and silicon both belong to the group 14, but inspite of the stoichiometric similarity, the dioxides, (i.e., carbon dioxide and silicon dioxide), differ in their structures. Comment.

30. If a trivalent atom replaces a few silicon atoms in three dimensional network of silicon dioxide, what would be the type of charge on overall structure?

31. When BCl_3 is treated with water, it hydrolyses and forms $[B[OH]_4]^-$ only whereas $AlCl_3$ in acidified aqueous solution forms $[Al(H_2O)_6]^{3+}$ ion. Explain what is the hybridisation of boron and aluminium in these species?

32. Aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character. A piece of aluminium foil is treated with dilute hydrochloric acid or dilute sodium hydroxide solution in a test tube and on bringing a burning matchstick near the mouth of the test tube, a pop sound indicates the evolution of hydrogen gas. The same activity when performed with concentrated nitric acid, reaction doesn't proceed. Explain the reason.

33. Explain the following :

(i) Gallium has higher ionisation enthalpy than aluminium.

(ii) Boron does not exist as B^{3+} ion.

(iii) Aluminium forms $[AlF_6]^{3-}$ ion but boron does not form $[BF_6]^{3-}$ ion.

(iv) PbX_2 is more stable than PbX_4.

(v) Pb^{4+} acts as an oxidising agent but Sn^{2+} acts as a reducing agent.

(vi) Electron gain enthalpy of chlorine is more negative as compared to fluorine.

(vii) $Tl(NO_3)_3$ acts as an oxidising agent.

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(viii) Carbon shows catenation property but lead does not.

(ix) BF_3 does not hydrolyse.

(x) Why does the element silicon, not form a graphite like structure whereas carbon does.

34. Identify the compounds A, X and Z in the following reactions :

(i) $A + 2HCl + 5H_2O \longrightarrow 2NaCl + X$

$$X \xrightarrow[370K]{\Delta} HBO_2 \xrightarrow[>370K]{\Delta} Z$$

35. Complete the following chemical equations :

$Z + 3\ LiAlH_4 \longrightarrow X + 3\ LiF + 3AlF_3$

$X + 6H_2O \longrightarrow Y + 6H_2$

$3X + 3O_2 \xrightarrow{\Delta} B_2O_3 + 3H_2O$

IV. Matching Type

In the following questions more than one correlation is possible between options of Column I and Column II. Make as many correlations as you can.

36. Match the species given in Column I with the properties mentioned in Column II.

Column I	Column II
(i) BF_4^-	(a) Oxidation state of central atom is +4
(ii) $AlCl_3$	(b) Strong oxidising agent
(iii) SnO	(c) Lewis acid
(iv) PbO_2	(d) Can be further oxidised
	(e) Tetrahedral shape

37. Match the species given in Column I with properties given in Column II.

Column I	Column II
(i) Diborane	(a) Used as a flux for soldering metals
(ii) Galluim	(b) Crystalline form of silica
(iii) Borax	(c) Banana bonds
(iv) Aluminosilicate	(d) Low melting, high boiling, useful for measuring high temperatures
(v) Quartz	(e) Used as catalyst in petrochemical industries

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38. Match the species given in Column I with the hybridisation given in Column II.

Column I	Column II
(i) Boron in $[B(OH)_4]^-$	(a) sp^2
(ii) Aluminium in $[Al(H_2O)_6]^{3+}$	(b) sp^3
(iii) Boron in B_2H_6	(c) sp^3d^2
(iv) Carbon in Buckminsterfullerene	
(v) Silicon in SiO_4^{4-}	
(vi) Germanium in $[GeCl_6]^{2-}$	

V. Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

39. ***Assertion (A):*** If aluminium atoms replace a few silicon atoms in three dimensional network of silicon dioxide, the overall structure acquires a negative charge.

Reason (R) : Aluminium is trivalent while silicon is tetravalent.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct

(iv) A is not correct but R is correct.

40. ***Assertion (A):*** Silicons are water repelling in nature.

Reason (R) : Silicons are organosilicon polymers, which have $(-R_2SiO-)$ as repeating unit.

(i) A and R both are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) A and R both are not true.

(iv) A is not true but R is true.

VI. Long Answer Type

41. Describe the general trends in the following properties of the elements in Groups 13 and 14.

(i) Atomic size

(ii) Ionisation enthalpy

(iii) Metallic character

(iv) Oxidation states

(v) Nature of halides

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42. Account for the following observations:

(i) $AlCl_3$ is a Lewis acid

(ii) Though fluorine is more electronegative than chlorine yet BF_3 is a weaker Lewis acid than BCl_3

(iii) PbO_2 is a stronger oxidising agent than SnO_2

(iv) The +1 oxidation state of thallium is more stable than its +3 state.

43. When aqueous solution of borax is acidified with hydrochloric acid, a white crystalline solid is formed which is soapy to touch. Is this solid acidic or basic in nature? Explain.

44. Three pairs of compounds are given below. Identify that compound in each of the pairs which has group 13 element in more stable oxidation state. Give reason for your choice. State the nature of bonding also.

(i) $TlCl_3$, TlCl

(ii) $AlCl_3$, AlCl

(iii) $InCl_3$, InCl

45. BCl_3 exists as monomer whereas $AlCl_3$ is dimerised through halogen bridging. Give reason. Explain the structure of the dimer of $AlCl_3$ also.

46. Boron fluoride exists as BF_3 but boron hydride doesn't exist as BH_3. Give reason. In which form does it exist? Explain its structure.

47. (i) What are silicones? State the uses of silicones.

(ii) What are boranes? Give chemical equation for the preparation of diborane.

48. A compound (A) of boron reacts with NMe_3 to give an adduct (B) which on hydrolysis gives a compound (C) and hydrogen gas. Compound (C) is an acid. Identify the compounds A, B and C. Give the reactions involved.

49. A nonmetallic element of group 13, used in making bullet proof vests is extremely hard solid of black colour. It can exist in many allotropic forms and has unusually high melting point. Its trifluoride acts as Lewis acid towards ammonia. The element exihibits maximum covalency of four. Identify the element and write the reaction of its trifluoride with ammonia. Explain why does the trifluoride act as a Lewis acid.

50. A tetravalent element forms monoxide and dioxide with oxygen. When air is passed over heated element (1273 K), producer gas is obtained. Monoxide of the element is a powerful reducing agent and reduces ferric oxide to iron. Identify the element and write formulas of its monoxide and dioxide. Write chemical equations for the formation of producer gas and reduction of ferric oxide with the monoxide.

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ANSWERS

I. Multiple Choice Questions (Type-I)

1. (iii)	2. (i)	3. (i)	4. (i)	5. (i)	6. (iii)
7. (ii)	8. (iii)	9. (iv)	10. (ii)	11. (i)	12. (ii)
13. (iv)	14. (iii)	15. (ii)			

II. Multiple Choice Questions (Type-II)

16. (i), (ii)	17. (ii), (iii)	18. (i), (ii)
19. (ii), (iii)	20. (i), (ii), (iv)	21. (ii), (iv)

III. Short Answer Type

23. Boric acid acts as Lewis acid in water by accepting a pair of electrons from a hydroxyl ion :

$B(OH)_3 + 2HOH \longrightarrow [B(OH)_4]^- + H_3O^+$

24. Species present in water is $[B(OH)_4]^-$. Boron is sp^3 hybridised.

25. BCl_3 and $AlCl_3$ being electron deficient due to incomplete octet of central metal atom behave as Lewis acids.

26. CCl_4 is a covalent compound. Hence, insoluble in water whereas $SiCl_4$ is soluble because Si atom in $SiCl_4$ can accomodate the lone pair of electrons obtained from oxygen atom of water molecule in *d*-orbitals.

27. (i) Very high Si-O bond enthalpy and ionic character of Si-O bond.

(ii) Vacant 3*d* orbitals are available on Si atom to accomodate electrons and expand coordination number upto 6.

29. [**Hint :** In CO_2, carbon is *sp* hybridised and it is a linear molecule. In SiO_2, Si is tetrahedrally bonded to four oxygen atoms.]

30. Negative

32. [**Hint :** Conc. HNO_3 renders aluminium passive by forming a protective oxide layer on the surface.]

34. A : $Na_2B_4O_7$ (Borax)
X : H_3BO_3
Z : B_2O_3

35. A : BF_3
X : B_2H_6
Y ; H_3BO_3

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IV. Matching Type

36. (i) → (e) (ii) → (c) (iii) → (d) (iv) → (a), (b)

37. (i)→ (c) (ii)→ (d) (iii)→(a) (iv)→(e) (v)→(b)

38. (i)→ (b), (ii) → (c), (iii) → (b), (iv) → (a) (v)→(b) (vi)→(c)

V. Assertion and Reason Type

39. (i) 40. (ii)

VI. Long Answer Type

45. [**Hint :** Absence of *d*-orbitals in boron.]

48. A = B_2H_6, B = $BH_3.NMe_3$, C = $B(OH)_3$ i.e. H_3BO_3.

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Unit

12

ORGANIC CHEMISTRY
SOME BASIC PRINCIPLES AND TECHNIQUES

I. Multiple Choice Questions (Type-I)

1. Which of the following is the correct IUPAC name?

(i) 3-Ethyl-4, 4-dimethylheptane

(ii) 4,4-Dimethyl-3-ethylheptane

(iii) 5-Ethyl-4, 4-dimethylheptane

(iv) 4,4-Bis(methyl)-3-ethylheptane

2. The IUPAC name for $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$ is _____.

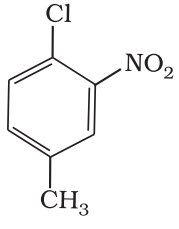
(i) 1-hydroxypentane-1,4-dione

(ii) 1,4-dioxopentanol

(iii) 1-carboxybutan-3-one

(iv) 4-oxopentanoic acid

3. The IUPAC name for



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(i) 1-Chloro-2-nitro-4-methylbenzene

(ii) 1-Chloro-4-methyl-2-nitrobenzene

(iii) 2-Chloro-1-nitro-5-methylbenzene

(iv) *m*-Nitro-*p*-chlorotoluene

4. Electronegativity of carbon atoms depends upon their state of hybridisation. In which of the following compounds, the carbon marked with asterisk is most electronegative?

(i) $CH_3 - CH_2 - {}^*CH_2 - CH_3$

(ii) $CH_3 - {}^*CH = CH - CH_3$

(iii) $CH_3 - CH_2 - C \equiv {}^*CH$

(iv) $CH_3 - CH_2 - CH = {}^*CH_2$

5. In which of the following, functional group isomerism is **not** possible?

(i) Alcohols

(ii) Aldehydes

(iii) Alkyl halides

(iv) Cyanides

6. The fragrance of flowers is due to the presence of some steam volatile organic compounds called essential oils. These are generally insoluble in water at room temperature but are miscible with water vapour in vapour phase. A suitable method for the extraction of these oils from the flowers is:

(i) Distillation

(ii) Crystallisation

(iii) Distillation under reduced pressure

(iv) Steam distillation

7. During hearing of a court case, the judge suspected that some changes in the documents had been carried out. He asked the forensic department to check the ink used at two different places. According to you which technique can give the best results?

(i) Column chromatography

(ii) Solvent extraction

(iii) Distillation

(iv) Thin layer chromatography

8. The principle involved in paper chromatography is

(i) Adsorption

(ii) Partition

(iii) Solubility

(iv) Volatility

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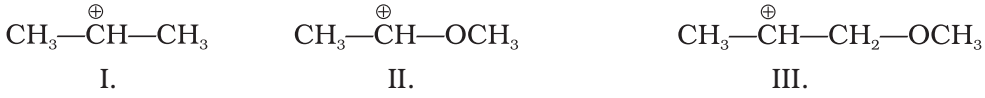
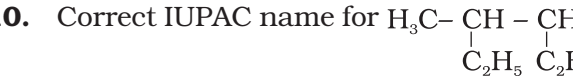
9. What is the correct order of decreasing stability of the following cations.



I. II. III.

(i) II > I > III
(ii) II > III > I
(iii) III > I > II
(iv) I > II > III

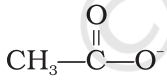
10. Correct IUPAC name for  is _____.

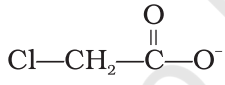
(i) 2- ethyl-3-methylpentane
(ii) 3,4- dimethylhexane
(iii) 2-*sec*-butylbutane
(iv) 2, 3-dimethylbutane

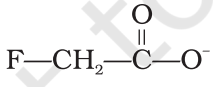
11. In which of the following compounds the carbon marked with asterisk is expected to have greatest positive charge?

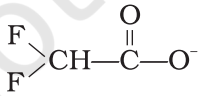
(i) $*CH_3—CH_2—Cl$
(ii) $*CH_3—CH_2—Mg^+Cl^-$
(iii) $*CH_3—CH_2—Br$
(iv) $*CH_3—CH_2—CH_3$

12. Ionic species are stabilised by the dispersal of charge. Which of the following carboxylate ion is the most stable?

(i) 

(ii) 

(iii) 

(iv) 

13. Electrophilic addition reactions proceed in two steps. The first step involves the addition of an electrophile. Name the type of intermediate formed in the first step of the following addition reaction.

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(i) 2° Carbanion

(ii) 1° Carbocation

(iii) 2° Carbocation

(iv) 1° Carbanion

14. Covalent bond can undergo fission in two different ways. The correct representation involving a heterolytic fission of CH_3—Br is

(i) $CH_3—Br \longrightarrow \overset{\oplus}{C}H_3 + Br^{\ominus}$

(ii) $CH_3—Br \longrightarrow \overset{\oplus}{C}H_3 + Br^{\ominus}$

(iii) $CH_3—Br \longrightarrow \overset{\ominus}{C}H_3 + Br^{\oplus}$

(iv) $CH_3—Br \longrightarrow \dot{C}H_3 + \dot{B}r$

15. The addition of HCl to an alkene proceeds in two steps. The first step is the attack of H^+ ion to $>C = C<$ portion which can be shown as

(i) $H^+ \rightarrow >C = \overset{\curvearrowright}{C}<$

(ii) $H^+ \leftarrow >C = C<$

(iii) $H^+ \quad >C = C<$

(iv) All of these are possible

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

16. Which of the following compounds contain all the carbon atoms in the same hybridisation state?

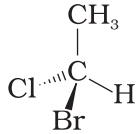
(i) H—C ≡ C—C ≡ C—H

(ii) CH_3—C ≡ C—CH_3

(iii) $CH_2 = C = CH_2$

(iv) $CH_2 = CH—CH = CH_2$

17. In which of the following representations given below spatial arrangement of group/ atom **different** from that given in structure 'A'?



(A)

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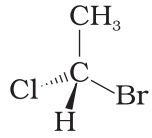
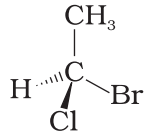
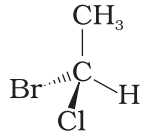
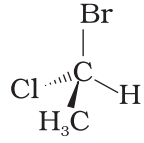
(i) 

(ii) 

(iii) 

(iv) 

18. Electrophiles are electron seeking species. Which of the following groups contain only electrophiles?

(i) BF_3 , NH_3 , H_2O

(ii) $AlCl_3$, SO_3 , NO_2^+

(iii) NO_2^+ , CH_3^+ , $CH_3 - \overset{+}{C} = O$

(iv) $C_2H_5^-$, $\dot{C}_2H_5$, $C_2H_5^+$

Note : Consider the following four compounds for answering questions 19 and 20.

I. $CH_3–CH_2–CH_2–CH_2–\overset{\overset{O}{\|}}{C}–H$

II. $CH_3–CH_2–CH_2–\overset{\overset{O}{\|}}{C}–CH_3$

III. $CH_3–CH_2–\underset{\underset{O}{\|}}{C}–CH_2–CH_3$

IV. $CH_3–\underset{\underset{CH_3}{|}}{CH}–CH_2–\underset{\underset{O}{\|}}{C}–H$

19. Which of the following pairs are position isomers?

(i) I and II

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(ii) II and III
(iii) II and IV
(iv) III and IV

20. Which of the following pairs are **not** functional group isomers?
(i) II and III
(ii) II and IV
(iii) I and IV
(iv) I and II

21. Nucleophile is a species that should have
(i) a pair of electrons to donate
(ii) positive charge
(iii) negative charge
(iv) electron deficient species

22. Hyperconjugation involves delocalisation of _____.
(i) electrons of carbon-hydrogen σ bond of an alkyl group directly attached to an atom of unsaturated system.
(ii) electrons of carbon-hydrogen σ bond of alkyl group directly attached to the positively charged carbon atom.
(iii) π-electrons of carbon-carbon bond
(iv) lone pair of electrons

III. Short Answer Type

Note : Consider structures I to VII and answer the questions 23–26.

I. $CH_3—CH_2—CH_2—CH_2—OH$

II. $CH_3—CH_2—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$

III. $CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}—CH_3$

IV. $CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—OH$

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V. $CH_3—CH_2—O—CH_2—CH_3$

VI. $CH_3—O—CH_2—CH_2—CH_3$

VII. $CH_3—O—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$

23. Which of the above compounds form pairs of metamers?

24. Identify the pairs of compounds which are functional group isomers.

25. Identify the pairs of compounds that represents position isomerism.

26. Identify the pairs of compounds that represents chain isomerism.

27. For testing halogens in an organic compound with $AgNO_3$ solution, sodium extract (Lassaigne's test) is acidified with dilute HNO_3. What will happen if a student acidifies the extract with dilute H_2SO_4 in place of dilute HNO_3?

28. What is the hybridisation of each carbon in $H_2C = C = CH_2$.

29. Explain, how is the electronegativity of carbon atoms related to their state of hybridisation in an organic compound?

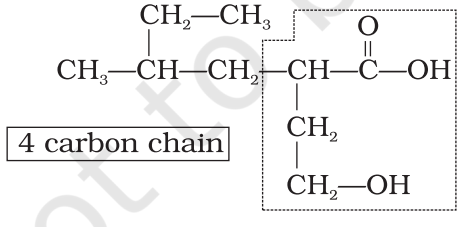
30. Show the polarisation of carbon-magnesium bond in the following structure.

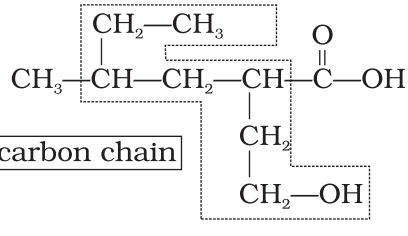
$CH_3—CH_2—CH_2—CH_2—Mg—X$

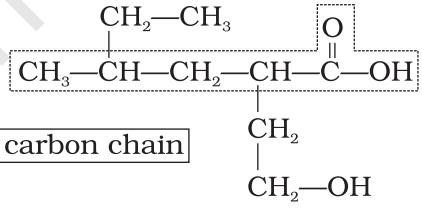
31. Compounds with same molecular formula but differing in their structures are said to be structural isomers. What type of structural isomerism is shown by

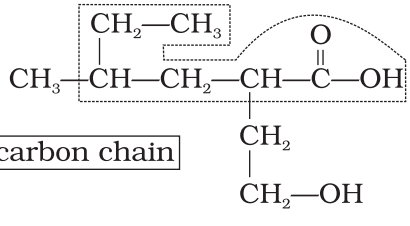
$CH_3—S—CH_2—CH_2—CH_3$ and $CH_3—S—CH(CH_3)_2$

32. Which of the following selected chains is correct to name the given compound according to IUPAC system.









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33. In DNA and RNA, nitrogen atom is present in the ring system. Can Kjeldahl method be used for the estimation of nitrogen present in these? Give reasons.

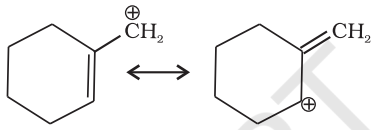
34. If a liquid compound decomposes at its boiling point, which method (s) can you choose for its purification. It is known that the compound is stable at low pressure, steam volatile and insoluble in water.

Note : Answer the questions 35 to 38 on the basis of information given below:

"Stability of carbocations depends upon the electron releasing inductive effect of groups adjacent to positively charged carbon atom involvement of neighbouring groups in hyperconjugation and resonance."

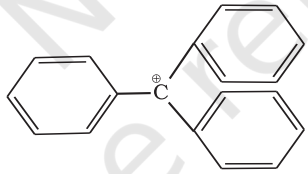
35. Draw the possible resonance structures for $CH_3—\ddot{O}—\overset{+}{C}H_2$ and predict which of the structures is more stable. Give reason for your answer.

36. Which of the following ions is more stable? Use resonance to explain your answer.



(A) (B)

37. The structure of triphenylmethyl cation is given below. This is very stable and some of its salts can be stored for months. Explain the cause of high stability of this cation.



38. Write structures of various carbocations that can be obtained from 2-methylbutane. Arrange these carbocations in order of increasing stability.

39. Three students, Manish, Ramesh and Rajni were determining the extra elements present in an organic compound given by their teacher. They prepared the Lassaigne's extract (L.E.) independently by the fusion of the compound with sodium metal. Then they added solid $FeSO_4$ and dilute sulphuric acid to a part of Lassaigne's extract. Manish and Rajni obtained prussian blue colour but Ramesh got red colour. Ramesh repeated the test with the same Lassaigne's extract, but again got red colour only. They were surprised and went to their teacher and told him about their observation. Teacher asked them to think over the reason for this. Can you help them by giving the reason for this observation. Also, write the chemical equations to explain the formation of compounds of different colours.

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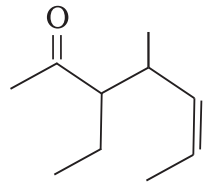
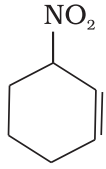
40. Name the compounds whose line formulae are given below :

(i) 

(ii) 

41. Write structural formulae for compounds named as-

(a) 1-Bromoheptane (b) 5-Bromoheptanoic acid

42. Draw the resonance structures of the following compounds;

(i) $CH_2 = CH—\ddot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}}:$

(ii) $CH_2 = CH—CH = CH_2$

(iii) $CH_2 = CH—\underset{\underset{H}{|}}{C} = O$

43. Identify the most stable species in the following set of ions giving reasons :

(i) $\overset{+}{C}H_3$, $\overset{+}{C}H_2Br$, $\overset{+}{C}HBr_2$, $\overset{+}{C}Br_3$

(ii) $\overset{\ominus}{C}H_3$, $\overset{\ominus}{C}H_2Cl$, $\overset{\ominus}{C}HCl_2$, $\overset{\ominus}{C}Cl_3$

44. Give three points of differences between inductive effect and resonance effect.

45. Which of the following compounds will not exist as resonance hybrid. Give reason for your answer :

(i) CH_3OH (ii) $R—CONH_2$ (iii) $CH_3CH = CHCH_2NH_2$

46. Why does SO_3 act as an electrophile?

47. Resonance structures of propenal are given below. Which of these resonating structures is more stable? Give reason for your answer.

$$\underset{\text{I}}{CH_2 = CH—CH = O} \longleftrightarrow \underset{\text{II}}{\overset{\oplus}{C}H_2—CH = CH—\overset{\ominus}{O}}$$

48. By mistake, an alcohol (boiling point 97°C) was mixed with a hydrocarbon (boiling point 68°C). Suggest a suitable method to separate the two compounds. Explain the reason for your choice.

49. Which of the two structures (A) and (B) given below is more stabilised by resonance? Explain.

CH_3COOH and $CH_3C\overset{\ominus}{O}O$

(A) (B)

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IV. Matching Type

In the following questions more than one correlation is possible between options of Column I and Column II. Make as many correlations as you can.

50. Match the type of mixture of compounds in Column I with the technique of separation/purification given in Column II.

	Column I		**Column II**
(i)	Two solids which have different solubilities in a solvent and which do not undergo reaction when dissolved in it.	(a)	Steam distillation
(ii)	Liquid that decomposes at its boiling point	(b)	Fractional distillation
(iii)	Steam volatile liquid	(c)	Simple distillation
(iv)	Two liquids which have boiling points close to each other	(d)	Distillation under reduced pressure
(v)	Two liquids with large difference in boiling points.	(e)	Crystallisation

51. Match the terms mentioned in Column I with the terms in Column II.

	Column I		**Column II**
(i)	Carbocation	(a)	Cyclohexane and 1- hexene
(ii)	Nucleophile	(b)	Conjugation of electrons of C–H σ bond with empty *p*-orbital present at adjacent positively charged carbon.
(iii)	Hyperconjugation	(c)	sp^2 hybridised carbon with empty *p*-orbital
(iv)	Isomers	(d)	Ethyne
(v)	*sp* hybridisation	(e)	Species that can receive a pair of electrons
(vi)	Electrophile	(f)	Species that can supply a pair of electrons

52. Match Column I with Column II.

	Column I		**Column II**
(i)	Dumas method	(a)	$AgNO_3$

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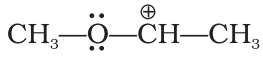
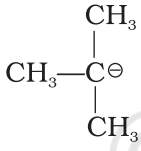
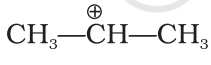
(ii)	Kjeldahl's method	(b)	Silica gel
(iii)	Carius method	(c)	Nitrogen gas
(iv)	Chromatography	(d)	Free radicals
(v)	Homolysis	(e)	Ammonium sulphate

53. Match the intermediates given in Column I with their probable structure in Column II.

	Column I		**Column II**
(i)	Free radical	(a)	Trigonal planar
(ii)	Carbocation	(b)	Pyramidal
(iii)	Carbanion	(c)	Linear

54. Match the ions given in Column I with their nature given in Column II.

	Column I		**Column II**
(i)		(a)	Stable due to resonance
(ii)		(b)	Destabilised due to inductive effect
(iii)		(c)	Stabilised by hyperconjugation
(iv)		(d)	A secondary carbocation

V. Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

55. ***Assertion (A) :*** Simple distillation can help in separating a mixture of propan-1-ol (boiling point 97°C) and propanone (boiling point 56°C).

Reason (R) : Liquids with a difference of more than 20°C in their boiling points can be separated by simple distillation.

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(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

56. ***Assertion (A) :*** Energy of resonance hybrid is equal to the average of energies of all canonical forms.

Reason (R) : Resonance hybrid cannot be presented by a single structure.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

57. ***Assertion (A) :*** Pent- 1- ene and pent- 2- ene are position isomers.

Reason (R) : Position isomers differ in the position of functional group or a substituent.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

58. ***Assertion (A) :*** All the carbon atoms in $H_2C = C = CH_2$ are sp^2 hybridised

Reason (R) : In this molecule all the carbon atoms are attached to each other by double bonds.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

59. ***Assertion (A) :*** Sulphur present in an organic compound can be estimated quantitatively by Carius method.

Reason (R) : Sulphur is separated easily from other atoms in the molecule and gets precipitated as light yellow solid.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

60. ***Assertion (A):*** Components of a mixture of red and blue inks can be separated by distributing the components between stationary and mobile phases in paper chromatography.

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Reason (R) : The coloured components of inks migrate at different rates because paper selectively retains different components according to the difference in their partition between the two phases.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

VI. Long Answer Type

61. What is meant by hybridisation? Compound $CH_2 = C = CH_2$ contains *sp* or sp^2 hybridised carbon atoms. Will it be a planar molecule?

62. Benzoic acid is a organic compound. Its crude sample can be purified by crystallisation from hot water. What characteristic differences in the properties of benzoic acid and the impurity make this process of purification suitable?

63. Two liquids (A) and (B) can be separated by the method of fractional distillation. The boiling point of liquid (A) is less than boiling point of liquid (B). Which of the liquids do you expect to come out first in the distillate? Explain.

64. You have a mixture of three liquids A, B and C. There is a large difference in the boiling points of A and rest of the two liquids i.e., B and C. Boiling point of liquids B and C are quite close. Liquid A boils at a higher temperature than B and C and boiling point of B is lower than C. How will you separate the components of the mixture. Draw a diagram showing set up of the apparatus for the process.

65. Draw a diagram of bubble plate type fractionating column. When do we require such type of a column for separating two liquids. Explain the principle involved in the separation of components of a mixture of liquids by using fractionating column. What industrial applications does this process have?

66. A liquid with high boiling point decomposes on simple distillation but it can be steam distilled for its purification. Explain how is it possible?

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ANSWERS

I. Multiple Choice Questions (Type-I)

1. (ii) 2. (iv) 3. (ii) 4. (iii) 5. (iii) 6. (iv)
7. (iv) 8. (ii) 9. (i) 10. (ii) 11. (i) 12. (iv)
13. (iii) 14. (ii) 15. (ii)

II. Multiple Choice Questions (Type-II)

16. (i), (iv) 17. (i), (iii), (iv) 18. (ii), (iii)
19. (ii) 20. (i), (iii) 21. (i), (iii)
22. (i), (ii)

III. Short Answer Type

27. White ppt. of Ag_2SO_4 will be formed.

29. Electronegativity increases with increasing '*s*' character.
$sp^3 < sp^2 < sp$

30. $CH_3—CH_2—CH_2—\overset{\delta-}{C}H_2—\overset{\delta+}{M}g—X$. Since electronegativity of carbon is more than magnesium it will behave as $CH_3—CH_2—CH_2—\ddot{\overset{-}{C}}H_2\ \overset{+}{M}gBr$.

31. Metamerism.

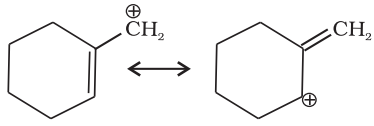
32. The four carbon chain. Selected chain should have maximum number of functional groups.

33. DNA and RNA have nitrogen in the heterocyclic rings. Nitrogen present in rings, azo groups and nitro groups cannot be removed as ammonia.

35. $CH_3—O—\overset{\oplus}{C}H_2$ (I) $\qquad$ $CH_3—\overset{\oplus}{\ddot{O}}=CH_2$ (II)

Structure II is more stable because every atom has complete octet.

36. Structure I is more stable due to resonance. (See resonance structure 'A' and 'B'). No resonance is possible in structure II.



(A) (B)

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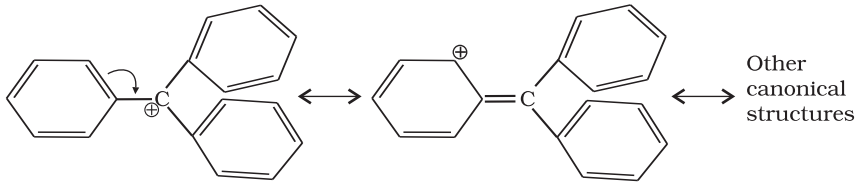
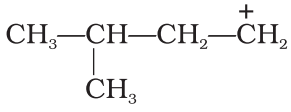
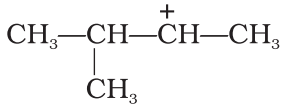
37. Stabilised due to nine possible canonical structures.



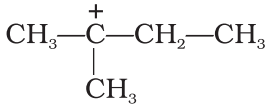
38. Four possible carbocations are



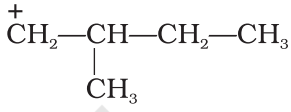
(I)



(II)



(III)



(IV)

Order of increasing stability I < IV < II < III

39. In Lassaigne's test SCN^- ions are formed due to the presence of sulphur and nitrogen both. These give red colour with Fe^{3+} ions. This happens when fusion is not carried out in the excess of sodium. With excess of sodium the thiocyanate ion, if formed, is decomposed as follows:

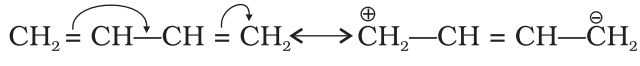
$$NaSCN + 2Na \longrightarrow NaCN + Na_2S$$

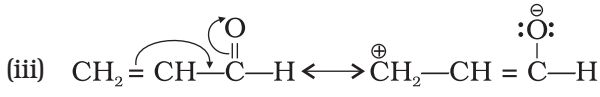
40. (i) 3-Ethyl-4-methylheptan-5-en-2-one
(ii) 3-Nitrocyclohex-1-ene.

41. (a) $CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2Br$

(b) $CH_3—CH_2—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_2—CH_2—CH_2—COOH$

42. (i)

(ii) 

(iii) 

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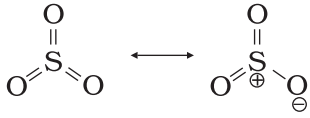
43. (i) $\overset{\oplus}{C}H_3$, The replacement of hydrogen by bromine increases positive charge on carbon atom and destabilises the species.

(ii) $\overset{\ominus}{C}—Cl_3$ is most stable because electronegativity of chlorine is more than hydrogen. On replacing hydrogen by chlorine, negative charge on carbon is reduced and species is stabilised.

44.

	Inductive effect		**Resonance effect**
(i)	Use σ-electrons	(a)	Use π- electrons or lone pair of electrons
(ii)	Move up to 3-carbon atoms	(b)	All along the length of conjugated system
(iii)	Slightly displaced electrons	(c)	Complete transfer of electrons

45. CH_3OH; Any possible contributing structure will have charge separation and incomplete octet of electrons on atoms. So the structure will be unstable due to high energy. e.g., $\overset{\oplus}{C}H_3\overset{\ominus}{O}H$.

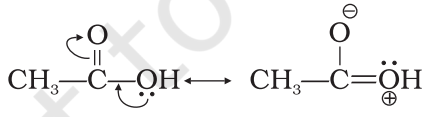
46. 

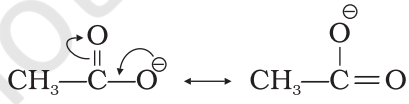
Three highly electronegative oxygen atoms are attached to sulphur atom. It makes sulphur atom electron deficient. Due to resonance also, sulphur acquires positive charge. Both these factors make SO_3 an electrophile.

47. I > II

48. Simple distillation can be used because the two compounds have a difference of more than 20° in their boiling points and both the liquids can be distilled without any decomposition.

49. Resonating structures are as follows:

(A) 

(B) 

Structure 'B' is more stabilised as it does not involve charge separation.

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IV. Matching Type

50. (i) → (e) (ii) → (d) (iii) → (a) (iv) → (b) (v) → (c)

51. (i) → (c) (ii) → (f) (iii) → (b) (iv) → (a) (v) → (d) (vi) → (e)

52. (i) → (c) (ii) → (e) (iii) → (a) (iv) → (b) (v) → (d)

53. (i) → (a), (ii) → (a) (iii) → (b)

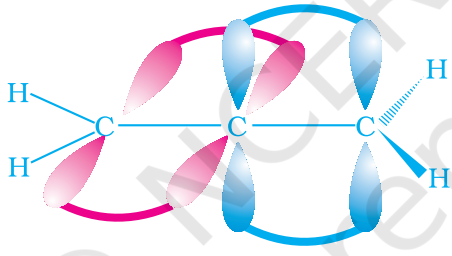
54. (i) → (a), (b), (d) (ii) → (b) (iii) → (b) (iv) → (c), (d)

V. Assertion and Reason Type

55. (i) 56. (iv) 57. (i) 58. (iv) 59. (iii) 60. (i)

VI. Long Answer Type

61. No. It is not a planar molecule.



Central carbon atom is *sp* hybridised and its two unhybridised *p*-orbitals are perpendicular to each other. The *p*-orbitals in one plane overlap with one of the *p*-orbital of left terminal carbon atom and the *p*-orbital in other plane overlaps with *p*-orbital of right side terminal carbon atom. This fixes the position of two terminal carbon atoms and the hydrogen atoms attached to them in planes perpendicular to each other. Due to this the pair of hydrogen atoms attached to terminal carbon atoms are present in different planes.

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Unit

13

HYDROCARBONS

I. Multiple Choice Questions (Type-I)

1. Arrange the following in decreasing order of their boiling points.

(A) *n*–butane (B) 2–methylbutane

(C) *n*-pentane (D) 2,2–dimethylpropane

(i) A > B > C > D

(ii) B > C > D > A

(iii) D > C > B > A

(iv) C > B > D > A

2. Arrange the halogens F_2 , Cl_2 , Br_2 , I_2 , in order of their increasing reactivity with alkanes.

(i) $I_2 < Br_2 < Cl_2 < F_2$

(ii) $Br_2 < Cl_2 < F_2 < I_2$

(iii) $F_2 < Cl_2 < Br_2 < I_2$

(iv) $Br_2 < I_2 < Cl_2 < F_2$

3. The increasing order of reduction of alkyl halides with zinc and dilute HCl is

(i) R–Cl < R–I < R–Br

ii) R–Cl < R–Br < R–I

(iii) R–I < R–Br < R–Cl

(iv) R–Br < R–I < R–Cl

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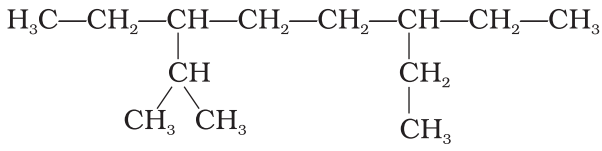
4. The correct IUPAC name of the following alkane is



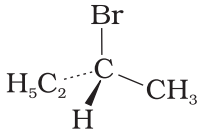
(i) 3,6 – Diethyl – 2 – methyloctane

(ii) 5 – Isopropyl – 3 – ethyloctane

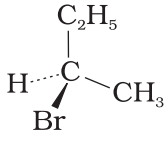
(iii) 3 – Ethyl – 5 – isopropyloctane

(iv) 3 – Isopropyl – 6 – ethyloctane

5. The addition of HBr to 1-butene gives a mixture of products A, B and C



(A)



(B)

(C)

The mixture consists of

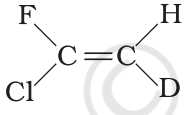
(i) A and B as major and C as minor products

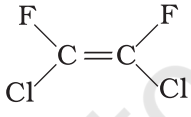
(ii) B as major, A and C as minor products

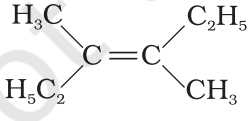
(iii) B as minor, A and C as major products

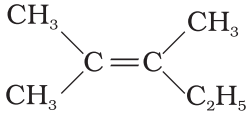
(iv) A and B as minor and C as major products

6. Which of the following will not show geometrical isomerism?

(i) 

(ii) 

(iii) 

(iv) 

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7. Arrange the following hydrogen halides in order of their decreasing reactivity with propene.

(i) HCl > HBr > HI

(ii) HBr > HI > HCl

(iii) HI > HBr > HCl

(iv) HCl > HI > HBr

8. Arrange the following carbanions in order of their decreasing stability.

(A) $H_3C - C \equiv C^-$ (B) $H - C \equiv C^-$ (C) $H_3C—\bar{C}H_2$

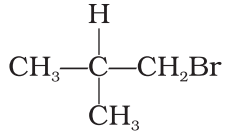
(i) A > B > C

(ii) B > A > C

(iii) C > B > A

(iv) C > A > B

9. Arrange the following alkyl halides in decreasing order of the rate of β– elimination reaction with alcoholic KOH.

(A)  (B) $CH_3—CH_2—Br$ (C) $CH_3—CH_2—CH_2—Br$

(i) A > B > C

(ii) C > B > A

(iii) B > C > A

(iv) A > C > B

10. Which of the following reactions of methane is incomplete combustion:

(i) $2CH_4 + O_2 \xrightarrow{Cu/523\ K/100\ atm} 2CH_3OH$

(ii) $CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$

(iii) $CH_4 + O_2 \longrightarrow C(s) + 2H_2O\ (l)$

(iv) $CH_4 + 2O_2 \longrightarrow CO_2\ (g) + 2H_2O\ (l)$

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

11. Some oxidation reactions of methane are given below. Which of them is/are controlled oxidation reactions?

(i) $CH_4\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O\ (l)$

(ii) $CH_4\ (g) + O_2\ (g) \longrightarrow C\ (s) + 2H_2O\ (l)$

(iii) $CH_4\ (g) + O_2\ (g) \xrightarrow{Mo_2O_3} HCHO + H_2O$

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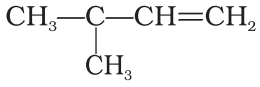
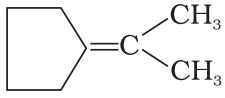
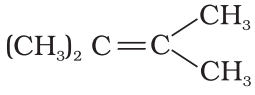
(iv) $2CH_4(g) + O_2(g) \xrightarrow{Cu/523/100\ atm} 2CH_3OH$

12. Which of the following alkenes on ozonolysis give a mixture of ketones only?

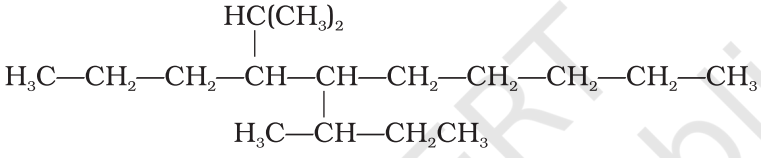
(i) $CH_3—CH=CH—CH_3$

(ii) 

(iii) 

(iv) 

13. Which are the correct IUPAC names of the following compound?



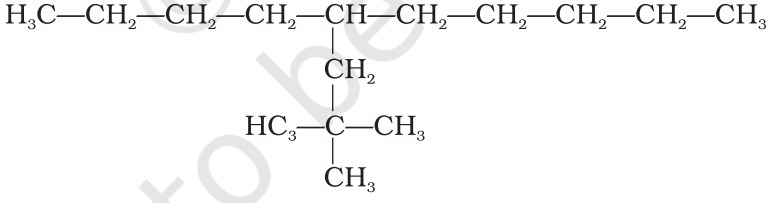
(i) 5– Butyl – 4– isopropyldecane

(ii) 5– Ethyl – 4– propyldecane

(iii) 5– *sec*-Butyl – 4– *iso*-propyldecane

(iv) 4–(1-methylethyl)– 5 – (1-methylpropyl)-decane

14. Which are the correct IUPAC names of the following compound?



(i) 5 – (2′, 2′–Dimethylpropyl)-decane

(ii) 4 – Butyl – 2,2– dimethylnonane

(iii) 2,2– Dimethyl – 4– pentyloctane

(iv) 5 – *neo*-Pentyldecane

15. For an electrophilic substitution reaction, the presence of a halogen atom in the benzene ring _____.

(i) deactivates the ring by inductive effect

(ii) deactivates the ring by resonance

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(iii) increases the charge density at ortho and para position relative to meta position by resonance

(iv) directs the incoming electrophile to meta position by increasing the charge density relative to ortho and para position.

16. In an electrophilic substitution reaction of nitrobenzene, the presence of nitro group _____.

(i) deactivates the ring by inductive effect.

(ii) activates the ring by inductive effect.

(iii) decreases the charge density at ortho and para position of the ring relative to meta position by resonance.

(iv) increases the charge density at meta position relative to the ortho and para positions of the ring by resonance.

17. Which of the following are correct?

(i) $CH_3—O—\overset{\oplus}{C}H_2$ is more stable than $CH_3—\overset{\oplus}{C}H_2$

(ii) $(CH_3)_2\overset{\oplus}{C}H$ is less stable than $CH_3—CH_2—\overset{\oplus}{C}H_2$

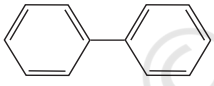
(iii) $CH_2=CH—\overset{\oplus}{C}H_2$ is more stable than $CH_3—CH_2—\overset{\oplus}{C}H_2$

(iv) $CH_2=\overset{\oplus}{C}H$ is more stable than $CH_3—\overset{\oplus}{C}H_2$

18. Four structures are given in options (i) to (iv). Examine them and select the aromatic structures.

(i)

(ii)

(iii) 

(iv)

19. The molecules having dipole moment are _____.

(i) 2,2-Dimethylpropane

(ii) *trans*-Pent-2-ene

(iii) *cis*-Hex-3-ene

(iv) 2, 2, 3, 3 - Tetramethylbutane.

III. Short Answer Type

20. Why do alkenes prefer to undergo electrophilic addition reaction while arenes prefer electrophilic substitution reactions? Explain.

21. Alkynes on reduction with sodium in liquid ammonia form trans alkenes. Will the butene thus formed on reduction of 2-butyne show the geometrical isomerism?

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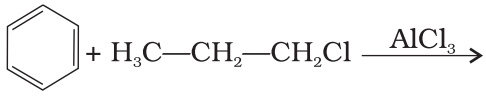
22. Rotation around carbon-carbon single bond of ethane is not completely free. Justify the statement.

23. Draw Newman and Sawhorse projections for the eclipsed and staggered conformations of ethane. Which of these conformations is more stable and why?

24. The intermediate carbocation formed in the reactions of HI, HBr and HCl with propene is the same and the bond energy of HCl, HBr and HI is 430.5 kJ mol^{-1}, 363.7 kJ mol^{-1} and 296.8 kJ mol^{-1} respectively. What will be the order of reactivity of these halogen acids?

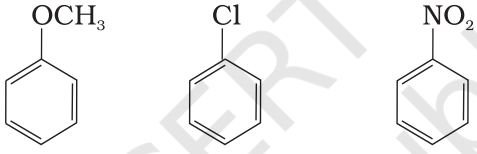
25. What will be the product obtained as a result of the following reaction and why?



26. How will you convert benzene into (i) *p* – nitrobromobenzene

(ii) *m* – nitrobromobenzene

27. Arrange the following set of compounds in the order of their decreasing relative reactivity with an electrophile.Give reason.

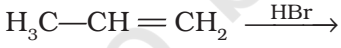


28. Despite their - I effect, halogens are *o*- and *p*-directing in haloarenes. Explain.

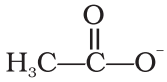
29. Why does presence of a nitro group make the benzene ring less reactive in comparison to the unsubstituted benzene ring. Explain.

30. Suggest a route for the preparation of nitrobenzene starting from acetylene?

31. Predict the major product (s) of the following reactions and explain their formation.



32. Nucleophiles and electrophiles are reaction intermediates having electron rich and electron deficient centres respectively. Hence, they tend to attack electron deficient and electron rich centres respectively. Classify the following species as electrophiles and nucleophiles.

(i) H_3CO^- (ii)  (iii) $\dot{C}l$ (iv) $Cl_2C:$

(v) $(H_3C)_3C^+$ (vi) Br^- (vii) H_3COH (viii) R–NH–R

33. The relative reactivity of 1°, 2°, 3° hydrogen's towards chlorination is 1 : 3.8 : 5. Calculate the percentages of all monochlorinated products obtained from 2-methylbutane.

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34. Write the structures and names of products obtained in the reactions of sodium with a mixture of 1-iodo-2-methylpropane and 2-iodopropane.

35. Write hydrocarbon radicals that can be formed as intermediates during monochlorination of 2-methylpropane? Which of them is more stable? Give reasons.

36. An alkane C_8H_{18} is obtained as the only product on subjecting a primary alkyl halide to Wurtz reaction. On monobromination this alkane yields a single isomer of a tertiary bromide. Write the structure of alkane and the tertiary bromide.

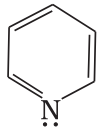
37. The ring systems having following characteristics are aromatic.

(i) Planar ring containing conjugated π bonds.

(ii) Complete delocalisation of the π–electrons in ring system i.e. each atom in the ring has unhybridised *p*-orbital, and

(iii) Presence of (4n+2) π–electrons in the ring where n is an integer (n = 0, 1, 2,.....) [Huckel rule].

Using this information classify the following compounds as aromatic/nonaromatic.

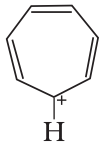


(A)

(B)

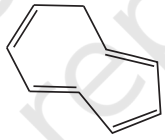
(C)

(D)



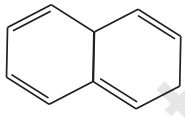
(E)

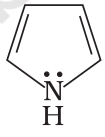
(F)

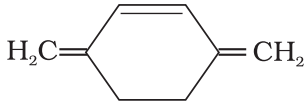


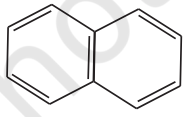
(G)

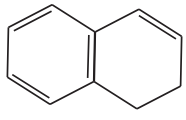
38. Which of the following compounds are aromatic according to Huckel's rule?

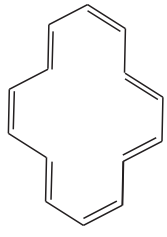
(A) 

(B) 

(C) 

(D) 

(E) 

(F) 

39. Suggest a route to prepare ethyl hydrogensulphate (CH_3–CH_2–OSO_2—OH) starting from ethanol (C_2H_5OH).

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IV. Matching Type

40. Match the reagent from Column I which on reaction with $CH_3—CH=CH_2$ gives some product given in Column II as per the codes given below :

	Column I		**Column II**
(i)	$O_3/Zn + H_2O$	(a)	Acetic acid and CO_2
(ii)	$KMnO_4/H^+$	(b)	Propan-1-ol
(iii)	$KMnO_4/OH^-$	(c)	Propan-2-ol
(iv)	H_2O/H^+	(d)	Acetaldehyde and formaldehyde
(v)	B_2H_6/NaOH and H_2O_2	(e)	Propane-1,2-diol

41. Match the hydrocarbons in Column I with the boiling points given in Column II.

	Column I		**Column II**
(i)	*n*–Pentane	(a)	282.5 K
(ii)	*iso*-Pentane	(b)	309 K
(iii)	*neo*-Pentane	(c)	301 K

42. Match the following reactants in Column I with the corresponding reaction products in Column II.

	Column I		**Column II**
(i)	Benzene + $Cl_2 \xrightarrow{AlCl_3}$	(a)	Benzoic acid
(ii)	Benzene + $CH_3Cl \xrightarrow{AlCl_3}$	(b)	Methyl phenyl ketone
(iii)	Benzene + $CH_3COCl \xrightarrow{AlCl_3}$	(c)	Toluene
(iv)	Toluene $\xrightarrow{KMnO_4/NaOH}$	(d)	Chlorobenzene
		(e)	Benzene hexachloride

43. Match the reactions given in Column I with the reaction types in Column II.

	Column I		**Column II**
(i)	$CH_2=CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2OH$	(a)	Hydrogenation
(ii)	$CH_2=CH_2 + H_2 \xrightarrow{Pd} CH_3—CH_3$	(b)	Halogenation
(iii)	$CH_2=CH_2 + Cl_2 \longrightarrow Cl—CH_2—CH_2—Cl$	(c)	Polymerisation
(iv)	$3\,CH\equiv CH \xrightarrow[Heat]{Cu\ tube} C_6H_6$	(d)	Hydration
		(e)	Condensation

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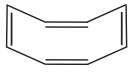
V. Assertion and Reason Type

In the following questions a statement of assertion (A) followed by a statement of reason (R) is given. Choose the correct option out of the choices given below each question.

44. ***Assertion (A) :*** The compound cyclooctane has the following structural formula :



It is cyclic and has conjugated 8π-electron system but it is not an aromatic compound.

Reason (R) : (4n + 2) π electrons rule does not hold good and ring is not planar.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

45. ***Assertion (A) :*** Toluene on Friedal Crafts methylation gives *o*– and *p*–xylene.

Reason (R) : CH_3-group bonded to benzene ring increases electron density at *o*– and *p*– position.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

46. ***Assertion (A) :*** Nitration of benzene with nitric acid requires the use of concentrated sulphuric acid.

Reason (R) : The mixture of concentrated sulphuric acid and concentrated nitric acid produces the electrophile, NO_2^+.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

47. ***Assertion (A) :*** Among isomeric pentanes, 2, 2-dimethylpentane has highest boiling point.

Reason (R) : Branching does not affect the boiling point.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

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VI. Long Answer Type

48. An alkyl halide $C_5H_{11}Br$ (A) reacts with ethanolic KOH to give an alkene 'B', which reacts with Br_2 to give a compound 'C', which on dehydrobromination gives an alkyne 'D'. On treatment with sodium metal in liquid ammonia one mole of 'D' gives one mole of the sodium salt of 'D' and half a mole of hydrogen gas. Complete hydrogenation of 'D' yields a straight chain alkane. Identify A,B, C and D. Give the reactions invovled.

49. 896 mL vapour of a hydrocarbon 'A' having carbon 87.80% and hydrogen 12.19% weighs 3.28g at STP. Hydrogenation of 'A' gives 2-methylpentane. Also 'A' on hydration in the presence of H_2SO_4 and $HgSO_4$ gives a ketone 'B' having molecular formula $C_6H_{12}O$. The ketone 'B' gives a positive iodoform test. Find the structure of 'A' and give the reactions involved.

50. An unsaturated hydrocarbon 'A' adds two molecules of H_2 and on reductive ozonolysis gives butane-1,4-dial, ethanal and propanone. Give the structure of 'A', write its IUPAC name and explain the reactions involved.

51. In the presence of peroxide addition of HBr to propene takes place according to anti Markovnikov's rule but peroxide effect is not seen in the case of HCl and HI. Explain.

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ANSWERS

I. Multiple Choice Questions (Type-I)

1. (iv) 2. (i) 3. (ii) 4. (i) 5. (i) 6. (iv)

7. (iii) 8. (ii) 9. (iv) 10. (iii)

II. Multiple Choice Questions (Type-II)

11. (iii), (iv) 12. (iii), (iv) 13. (iii), (iv)

14. (i), (iv) 15. (i), (iii) 16. (i), (iii)

17. (i), (iii) 18. (i), (iii) 19. (ii), (iii)

III. Short Answer Type

20. Both alkenes and arenes are electron-rich. Therefore undergo electrophilic reactions. Olefins undergo addition reactions because addition of a reagent to an olefin gives a more stable product as sp^2 hybridisation changes to sp^3 hybridisation. Addition to the double bond of an arene would give a product with less or no resonance stability hence addition is difficult arenes. On the other hand in substitution reaction resonance stabilisation is retained therefore, arenes undergo substitution reaction.

21. 2-Butene is capable of showing geometrical isomerism.

22. The rotation about C—C bond is restricted because of repulsion between electron cloud of C—H bonds on either carbon atoms.

24. Bond dissociation energy is least for HI and maximum for HCl therefore, order of reactivity will be HI > HBr > HCl.

25. Propyl chloride forms less stable $CH_3—CH_2—\overset{\oplus}{C}H_2$ carbocation with anhydrous $AlCl_3$ which rearranges to a more stable $CH_3—\overset{\oplus}{C}H—CH_3$ carbocation and gives isopropylbenzene as the product of the reaction.

27. The +R effect of $—OCH_3$ > —Cl and $—NO_2$ has a – R effect. Relative reactivity of the substituted benzene rings is as follows :

$C_6H_5—OCH_3 > C_6H_5—Cl > C_6H_5–NO_2$

28. Halogens attached to benzene rings exert –I and +R effect. +R effect dominates –I effect and increases the electron density at ortho and para positions of the benzene ring with respect to halogens.

33. 2-Methyl butane is $CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—CH_3$. Possible compounds are A, B and C given below :

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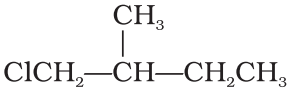
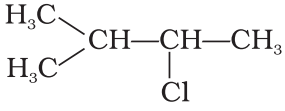


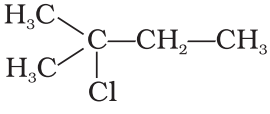
A (1°)

Nine possibilities for compound 'A' because nine methyl hydrogens are present in 2-methylbutane.



B (2°)

Two possibilities for 'B' compound because two CH hydrogens are present in 2-methylbutane.



C (3°)

Only one possibility for 'C' compound because one CH hydrogen is present in 2-methylbutane.

Relative amounts of A, B and C compounds = number of hydrogen × relative reactivity

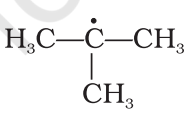
	A (1°)	**B (2°)**	**C (3°)**
Relative amount	9×1= 9	2×3.8 = 7.6	1×5=5

Total Amount of monohaloginated compounds = 9 + 7.6 + 5 = 21.6

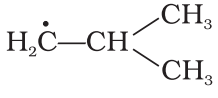
$$\text{Percentage of A} = \frac{9}{21.6} \times 100 = 41.7\%$$

$$\text{Percentage of B} = \frac{7.6}{21.6} \times 100 = 35.2\%$$

$$\text{Percentage of C} = \frac{5}{21.6} \times 100 = 23.1\%$$

35. 

I



II

Radical I is tertiary where as radical II is primary. Radical I is more stable due to hyperconjugation.

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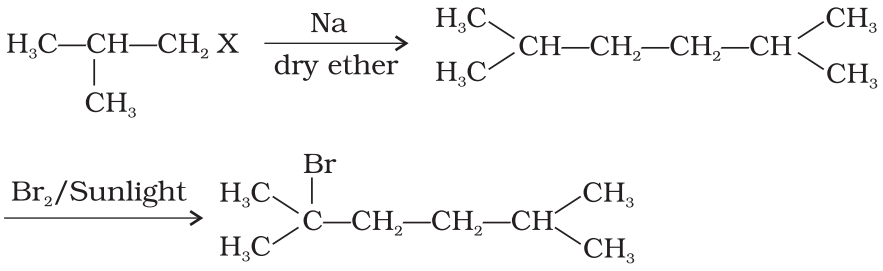
36. 

37. A = Planar ring, all atoms of the ring sp^2 hybridised, has six delocalised π electrons, follows Huckel rule. It is aromatic.

B = Has six π electrons, but the delocalisation stops at sp^3 hybridised CH_2- carbon. Hence, not aromatic.

C = Six delocalised π-electrons (4 π electrons + 2 unshared electrons on negatively charged carbon) in a planar ring, follows Huckel's rule. It is aromatic.

D = Has only four delocalised π-electrons. It is non aromatic.

E = Six delocalised π-electrons follows Huckel's rule. π electrons are in sp^2 hybridised orbitals, conjugation all over the ring because of positively charged carbon. The ring is planar hence is aromatic.

F = Follows Huckel's rule, has 2 π electrons i.e. (4n+2) π-electrons where (n=0), delocalised π-electrons. It is aromatic.

G = 8π electrons, does not follow Huckel's rule i.e., (4n+2) π-electrons rule. It is not aromatic.

38. A = Has 8π electrons, does not follow Huckel rule. Orbitals of one carbon atom are not in conjugation. It is not aromatic.

B = Has 6π delocalised electrons. Hence, is aromatic.

C = Has 6π electrons in conjugation but not in the ring. Non aromatic.

D = 10π electrons in planar rings, aromatic.

E = Out of 8π electrons it has delocalised 6π electrons in one six membered planar ring, which follows Huckel's rule due to which it will be aromatic.

F = 14 π electrons are in conjugation and are present in a ring. Huckel's rule is being followed. Compound will be aromatic if ring is planar.

IV. Matching Type

40. (i) → (d) (ii) → (a) (iii) → (e) (iv) → (c) (v) → (b)

41. (i) → (b) (ii) → (c) (iii) → (a)

42. (i) → (d) (ii) → (c) (iii) → (b) (iv) → (a)

43. (i) → (d) (ii) → (a) (iii) → (b) (iv) → (c)

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V. Assertion and Reason Type

44. (i) 45. (i) 46. (i) 47. (iii)

VI. Long Answer Type

48. $C_5H_{11}Br \xrightarrow{\text{alc.KOH}} \underset{(B)}{\text{Alkene } (C_5H_{10})} \xrightarrow{Br_2 \text{ in } CS_2} \underset{(C)}{C_5H_{10}Br_2}$

(A)

$\xrightarrow[-2HBr]{\text{Alc.KOH}} \underset{\text{D (Alkyne)}}{C_5H_8} \xrightarrow{\text{Na–liq.NH}_3} \underset{\text{Sodium alkylide}}{C_5H_7\text{–Na}} + \frac{1}{2}H_2$

The reactions suggest that (D) is a terminal alkyne. This means triple bond is at the end of the chain. It could be either (I) or (II).

$CH_3\text{—}CH_2\text{—}CH_2\text{—}CH_2\equiv CH$ (I)

$CH_3\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}C\equiv CH$ (II)

Since alkyne 'D' on hydrogenation yields straight chain alkane, therefore structure I is the structure of alkyne (D).

Hence, the structures of A, B and C are as follows :

(A) $CH_3\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2Br$

(B) $CH_3\text{—}CH_2\text{—}CH_2\text{—}CH = CH_2$

(C) $CH_3\text{—}CH_2\text{—}CH_2\text{—}CH\,(Br)\text{—}CH_2Br$

49. *Step I*

896 mL vapour of C_xH_y (A) weighs 3.28 g

22700 mL vapour of C_xH_y (A) weighs $\frac{3.28 \times 22700}{896}$ g mol^{-1} = 83.1 g mol^{-1}

Step II

Element	*(%)*	*Atomic mass*	*Relative ratio*	*Relative no. of atoms*	*Simplest ratio*
C	87.8	12	7.31	1	3
H	12.19	1	12.19	1.66	4.98≈5

Empirical formula of 'A' C_3H_5

Empirical formula mass = 35 + 5 = 41 u

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{83.1}{41} = 2.02 \approx 2$$

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$\Rightarrow$ Molecular mass is double of the empirical formula mass.

$\therefore$ Molecular Formula is C_6H_{10}

Step III

$$\underset{\text{(A)}}{C_6H_{10}} \xrightarrow{2H_2} \text{2-methylpentane}$$

Structure of 2-methylpentane is $(CH_3)_2CH—CH_2—CH_2—CH_3$

Hence, the molecule has a five carbon chain with a methyl group at the second carbon atom.

'A' adds a molecule of H_2O in the presence of Hg^{2+} and H^+, it should be an alkyne. Two possible structures for 'A' are :

$(CH_3)_2CH—C\equiv C—CH_3$ (I) or $(CH_3)_2CH—CH_2—C\equiv CH$ (II)

Since the ketone (B) gives a positive iodoform test, it should contain a $—COCH_3$ group. Hence the structure of ketone is as follows :

$(CH_3)_2CH—CH_2—CO—CH_3$

Therefore structure of alkyne is II.

50. Two molecules of hydrogen add on 'A' this shows that 'A' is either an alkadiene or an alkyne.

On reductive ozonolysis 'A' gives three fragments, one of which is dialdehyde. Hence, the molecule has broken down at two sites. Therefore, 'A' has two double bonds. It gives the following three fragments :

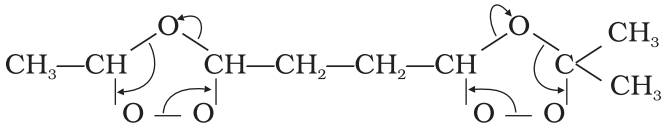
$OHC—CH_2—CH_2—CHO$, CH_3CHO and $CH_3—CO—CH_3$

Hence, its structure as deduced from the three fragments must be

$CH_3—CH=CH—CH_2—CH_2—CH=C(CH_3)—CH_3$

(A)

Reactions

(A) $\xrightarrow{\text{Ozone}}$ 

$\xrightarrow{Zn/H_2O}$ $CH_3—CHO + OHC—CH_2—CH_2—CHO + O=C(CH_3)_2$

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Unit

14

ENVIRONMENTAL CHEMISTRY

I. Multiple Choice Questions (Type-I)

1. Which of the following gases is not a green house gas?

(i) CO

(ii) O_3

(iii) CH_4

(iv) H_2O vapour

2. Photochemical smog occurs in warm, dry and sunny climate. One of the following is not amongst the components of photochemical smog, identify it.

(i) NO_2

(ii) O_3

(iii) SO_2

(iv) Unsaturated hydrocarbon

3. Which of the following statements is **not** true about classical smog?

(i) Its main components are produced by the action of sunlight on emissions of automobiles and factories.

(ii) Produced in cold and humid climate.

(iii) It contains compounds of reducing nature.

(iv) It contains smoke, fog and sulphur dioxide.

4. Biochemical Oxygen Demand, (BOD) is a measure of organic material present in water. BOD value less than 5 ppm indicates a water sample to be _____.

(i) rich in dissolved oxygen.

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(ii) poor in dissolved oxygen.

(iii) highly polluted.

(iv) not suitable for aquatic life.

5. Which of the following statements is wrong?

(i) Ozone is not responsible for green house effect.

(ii) Ozone can oxidise sulphur dioxide present in the atmosphere to sulphur trioxide.

(iii) Ozone hole is thinning of ozone layer present in stratosphere.

(iv) Ozone is produced in upper stratosphere by the action of UV rays on oxygen.

6. Sewage containing organic waste should not be disposed in water bodies because it causes major water pollution. Fishes in such a polluted water die because of

(i) Large number of mosquitoes.

(ii) Increase in the amount of dissolved oxygen.

(iii) Decrease in the amount of dissolved oxygen in water.

(iv) Clogging of gills by mud.

7. Which of the following statements about photochemical smog is wrong?

(i) It has high concentration of oxidising agents.

(ii) It has low concentration of oxidising agent.

(iii) It can be controlled by controlling the release of NO_2, hydrocarbons, ozone etc.

(iv) Plantation of some plants like pinus helps in controlling photochemical smog.

8. The gaseous envelope around the earth is known as atmosphere. The lowest layer of this is extended upto 10 km from sea level, this layer is _____.

(i) Stratosphere

(ii) Troposphere

(iii) Mesosphere

(iv) Hydrosphere

9. Dinitrogen and dioxygen are main constituents of air but these do not react with each other to form oxides of nitrogen because _____.

(i) the reaction is endothermic and requires very high temperature.

(ii) the reaction can be initiated only in presence of a catalyst.

(iii) oxides of nitrogen are unstable.

(iv) N_2 and O_2 are unreactive.

10. The pollutants which come directly in the air from sources are called primary pollutants. Primary pollutants are sometimes converted into secondary pollutants. Which of the following belongs to secondary air pollutants?

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(i) CO

(ii) Hydrocarbon

(iii) Peroxyacetyl nitrate

(iv) NO

11. Which of the following statements is correct?

(i) Ozone hole is a hole formed in stratosphere from which ozone oozes out.

(ii) Ozone hole is a hole formed in the troposphere from which ozone oozes out.

(iii) Ozone hole is thinning of ozone layer of stratosphere at some places.

(iv) Ozone hole means vanishing of ozone layer around the earth completely.

12. Which of the following practices will **not** come under green chemistry?

(i) If possible, making use of soap made of vegetable oils instead of using synthetic detergents.

(ii) Using H_2O_2 for bleaching purpose instead of using chlorine based bleaching agents.

(iii) Using bicycle for travelling small distances instead of using petrol/ diesel based vehicles.

(iv) Using plastic cans for neatly storing substances.

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

13. Which of the following conditions shows the polluted environment.

(i) pH of rain water is 5.6.

(ii) amount of carbondioxide in the atmosphere is 0.03%.

(iii) biochemical oxygen demand 10 ppm.

(iv) eutrophication.

14. Phosphate containing fertilisers cause water pollution. Addition of such compounds in water bodies causes _____.

(i) enhanced growth of algae.

(ii) decrease in amount of dissolved oxygen in water.

(iii) deposition of calcium phosphate.

(iv) increase in fish population.

15. The acids present in acid rain are _____.

(i) Peroxyacetylnitrate

(ii) H_2CO_3

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(iii) HNO_3

(iv) H_2SO_4

16. The consequences of global warming may be _____.

(i) increase in average temperature of the earth

(ii) melting of Himalayan Glaciers.

(iii) increased biochemical oxygen demand.

(iv) eutrophication.

III. Short Answer Type

17. Green house effect leads to global warming. Which substances are responsible for green house effect?

18. Acid rain is known to contain some acids. Name these acids and where from they come in rain?

19. Ozone is a toxic gas and is a strong oxidising agent even then its presence in the stratosphere is very important. Explain what would happen if ozone from this region is completely removed?

20. Dissolved oxygen in water is very important for aquatic life. What processes are responsible for the reduction of dissolved oxygen in water?

21. On the basis of chemical reactions involved, explain how do chlorofluorocarbons cause thinning of ozone layer in stratosphere.

22. What could be the harmful effects of improper management of industrial and domestic solid waste in a city?

23. During an educational trip, a student of botany saw a beautiful lake in a village. She collected many plants from that area. She noticed that villagers were washing clothes around the lake and at some places waste material from houses was destroying its beauty.

After few years, she visited the same lake again. She was surprised to find that the lake was covered with algae, stinking smell was coming out and its water had become unusable. Can you explain the reason for this condition of the lake?

24. What are biodegradable and non-biodegradable pollutants?

25. What are the sources of dissolved oxygen in water?

26. What is the importance of measuring BOD of a water body?

27. Why does water covered with excessive algal growth become polluted?

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28. A factory was started near a village. Suddenly villagers started feeling the presence of irritating vapours in the village and cases of headache, chest pain, cough, dryness of throat and breathing problems increased. Villagers blamed the emissions from the chimney of the factory for such problems. Explain what could have happened. Give chemical reactions for the support of your explanation.

29. Oxidation of sulphur dioxide into sulphur trioxide in the absence of a catalyst is a slow process but this oxidation occurs easily in the atmosphere. Explain how does this happen. Give chemical reactions for the conversion of SO_2 into SO_3.

30. From where does ozone come in the photochemical smog?

31. How is ozone produced in stratosphere?

32. Ozone is a gas heavier than air. Why does ozone layer not settle down near the earth?

33. Some time ago formation of polar stratospheric clouds was reported over Antarctica. Why were these formed? What happens when such clouds break up by warmth of sunlight?

34. A person was using water supplied by Municipality. Due to shortage of water he started using underground water. He felt laxative effect. What could be the cause?

IV. Matching Type

In the following questions more than one option of Column I and Column II may match.

35. Match the terms given in Column I with the compounds given in Column II.

	Column I		**Column II**
(i)	Acid rain	(a)	$CHCl_2 - CHF_2$
(ii)	Photochemical smog	(b)	CO
(iii)	Combination with haemoglobin	(c)	CO_2
(iv)	Depletion of ozone layer	(d)	SO_2
		(e)	Unsaturated hydrocarbons

36. Match the pollutant(s) in Column I with the effect(s) in Column II.

	Column I		**Column II**
(i)	Oxides of sulphur	(a)	Global warming
(ii)	Nitrogen dioxide	(b)	Damage to kidney

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(iii)	Carbon dioxide	(c)	'Blue baby' syndrome
(iv)	Nitrate in drinking water	(d)	Respiratory diseases
(v)	Lead	(e)	Red haze in traffic and congested areas

37. Match the activity given in Column I with the type of pollution created by it given in Column II.

	Column I (Activity)		**Column II (Effect)**
(i)	Releasing gases to the atmosphere after burning waste material containing sulphur.	(a)	Water pollution
(ii)	Using carbamates as pesticides	(b)	Photochemical smog, damage to plant life, corrosion to building material, induce breathing problems, water pollution
(iii)	Using synthetic detergents for washing clothes	(c)	Damaging ozone layer
(iv)	Releasing gases produced by automobiles and factories in the atmosphere.	(d)	May cause nerve diseases in human.
(v)	Using chlorofluorocarbon compounds for cleaning computer parts	(e)	Classical smog, acid rain, water pollution, induce breathing problems, damage to buildings, corrosion of metals.

38. Match the pollutants given in Column I with their effects given in Column II.

	Column I		**Column II**
(i)	Phosphate fertilisers in water	(a)	BOD level of water increases
(ii)	Methane in air	(b)	Acid rain
(iii)	Synthetic detergents in water	(c)	Global warming
(iv)	Nitrogen oxides in air	(d)	Eutrophication

V. Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

39. ***Assertion (A):*** Green house effect was observed in houses used to grow plants and these are made of green glass.

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Reason (R) : Green house name has been given because glass houses are made of green glass.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

40. ***Assertion (A) :*** The pH of acid rain is less than 5.6.

Reason (R) : Carbon dioxide present in the atmosphere dissolves in rain water and forms carbonic acid.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

41. ***Assertion (A) :*** Photochemical smog is oxidising in nature.

Reason (R) : Photochemical smog contains NO_2 and O_3, which are formed during the sequence of reactions.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

42. ***Assertion (A) :*** Carbon dioxide is one of the important greenhouse gases.

Reason (R) : It is largely produced by respiratory function of animals and plants.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

43. ***Assertion (A) :*** Ozone is destroyed by solar radiation in upper stratosphere.

Reason (R) : Thinning of the ozone layer allows excessive UV radiations to reach the surface of earth.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

44. ***Assertion (A) :*** Excessive use of chlorinated synthetic pesticides causes soil and water pollution.

Reason (R) : Such pesticides are non-biodegradable.

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(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

45. ***Assertion (A) :*** If BOD level of water in a reservoir is less than 5 ppm it is highly polluted.

Reason (R) : High biological oxygen demand means low activity of bacteria in water.

(i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

VI. Long Answer Type

46. How can you apply green chemistry for the following :

(i) to control photochemical smog.

(ii) to avoid use of halogenated solvents in drycleaning and that of chlorine in bleaching.

(iii) to reduce use of synthetic detergents.

(iv) to reduce the consumption of petrol and diesel.

47. Green plants use carbon dioxide for photosynthesis and return oxygen to the atmosphere, even then carbon dioxide is considered to be responsible for green house effect. Explain why?

48. Explain how does green house effect cause global warming.

49. A farmer was using pesticides on his farm. He used the produce of his farm as food for rearing fishes. He was told that fishes were not fit for human consumption because large amount of pesticides had accumulated in the tissues of fishes. Explain how did this happen?

50. For dry cleaning, in the place of tetrachloroethane, liquefied carbon dioxide with suitable detergent is an alternative solvent. What type of harm to the environment will be prevented by stopping use of tetrachloroethane? Will use of liquefied carbon dioxide with detergent be completely safe from the point of view of pollution? Explain.

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ANSWERS

I. Multiple Choice Questions (Type-I)

1. (i)	2. (iii)	3. (i)	4. (i)	5. (i)	6. (iii)
7. (ii)	8. (ii)	9. (i)	10. (iii)	11. (iii)	12. (iv)

II. Multiple Choice Questions (Type-II)

13. (iii), (iv) 14. (i), (ii) 15. (ii), (iii), (iv)

16. (i), (ii)

III. Short Answer Type

17. Trapping of heat by green house gases, namely carbon dioxide, methane, nitrous oxide, ozone and chlorofluorocarbons.

19. [**Hint :** Ozone prevents harmful UV radiations of the Sun from reaching to the Earth's surface, thereby it protects life from bad effects of UV radiations.]

21. CFC's are stable compounds. These undergo decomposition in presence of sunlight, as shown below :

Reactions: $CF_2Cl_2\,(g) \xrightarrow{UV} \dot{C}l\,(g) + \dot{C}F_2Cl\,(g)$

$\dot{C}l\,(g) + O_3\,(g) \longrightarrow Cl\dot{O}\,(g) + O_2\,(g)$

$Cl\dot{O}\,(g) + O\,(g) \longrightarrow \dot{C}l\,(g) + O_2\,(g)$

Chain reactions continue in which ozone layer is depleted.

23. [**Hint :** Process of eutrophication is responsible for this. Explain the effect of accumulation of phosphate from detergents and organic matter entering into the lake along with domestic waste.]

24. Biodegradable - which are decomposed by bacteria.

Non-biodegradable - which cannot be decomposed by bacteria.

25. Sources of dissolved oxygen in water

(i) Photosynthesis

(ii) Natural aeration

(iii) Mechanical aeration

26. BOD is the measure of level of pollution caused by organic biodegradable material. Low value of BOD indicates that water contains less organic matter.

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IV. Matching Type

35. (i) → (c), (d) (ii) → (e), (d) (iii) → (b) (iv) → (a)

36. (i) → (d) (ii) → (e) (iii) → (a) (iv) → (c) (v) → (b)

37. (i) → (e) (ii) → (d) (iii) → (a) (iv) → (b) (v) → (c)

38. (i) → (a), (d) (ii) → (c) (iii) → (a) (iv) → (b)

V. Assertion and Reason Type

39. (iii) 40. (ii) 41. (i) 42. (ii) 43. (iv) 44. (i)

45. (iii)

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APPENDIX I

ELEMENTS, THEIR ATOMIC NUMBER AND MOLAR MASS

Element	Symbol	Atomic Number	Molar mass/ (g mol^{-1})
Actinium	Ac	89	227.03
Aluminium	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.75
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	210
Barium	Ba	56	137.34
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01
Bismuth	Bi	83	208.98
Bohrium	Bh	107	(264)
Boron	B	5	10.81
Bromine	Br	35	79.91
Cadmium	Cd	48	112.40
Caesium	Cs	55	132.91
Calcium	Ca	20	40.08
Californium	Cf	98	251.08
Carbon	C	6	12.01
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copper	Cu	29	63.54
Curium	Cm	96	247.07
Dubnium	Db	105	(263)
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(252)
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	(257.10)
Fluorine	F	9	19.00
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.61
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Hassium	Hs	108	(269)
Helium	He	2	4.00
Holmium	Ho	67	164.93
Hydrogen	H	1	1.0079
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lr	103	(262.1)
Lead	Pb	82	207.19
Lithium	Li	3	6.94
Lutetium	Lu	71	174.96
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Meitneium	Mt	109	(268)
Mendelevium	Md	101	258.10

Element	Symbol	Atomic Number	Molar mass/ (g mol^{-1})
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.18
Neptunium	Np	93	(237.05)
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.0067
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	16.00
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97
Platinum	Pt	78	195.09
Plutonium	Pu	94	(244)
Polonium	Po	84	210
Potassium	K	19	39.10
Praseodymium	Pr	59	140.91
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.04
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(261)
Samarium	Sm	62	150.35
Scandium	Sc	21	44.96
Seaborgium	Sg	106	(266)
Selenium	Se	34	78.96
Silicon	Si	14	28.08
Silver	Ag	47	107.87
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulphur	S	16	32.06
Tantalum	Ta	73	180.95
Technetium	Tc	43	(98.91)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92
Thallium	Tl	81	204.37
Thorium	Th	90	232.04
Thulium	Tm	69	168.93
Tin	Sn	50	118.69
Titanium	Ti	22	47.88
Tungsten	W	74	183.85
Ununbium	Uub	112	(277)
Ununnilium	Uun	110	(269)
Unununium	Uuu	111	(272)
Uranium	U	92	238.03
Vanadium	V	23	50.94
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.91
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

The value given in parenthesis is the molar mass of the isotope of largest known half-life.

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APPENDIX II

SOME USEFUL CONVERSION FACTORS

Common Unit of Mass and Weight

1 pound = 453.59 grams

1 pound = 453.59 grams = 0.45359 kilogram

1 kilogram = 1000 grams = 2.205 pounds

1 gram = 10 decigrams = 100 centigrams
= 1000 milligrams

1 gram = 6.022×10^{23} atomic mass units or u

1 atomic mass unit = 1.6606×10^{-24} gram

1 metric tonne = 1000 kilograms
= 2205 pounds

Common Unit of Volume

1 quart = 0.9463 litre

1 litre = 1.056 quarts

1 litre = 1 cubic decimetre = 1000 cubic centimetres = 0.001 cubic metre

1 millilitre = 1 cubic centimetre = 0.001 litre
= 1.056×10^{-3} quart

1 cubic foot = 28.316 litres = 29.902 quarts
= 7.475 gallons

Common Units of Energy

1 joule = 1×10^7 ergs

1 thermochemical calorie** = 4.184 joules
= 4.184×10^7 ergs
= 4.129×10^{-2} litre-atmospheres
= 2.612×10^{19} electron volts

1 ergs = 1×10^{-7} joule = 2.3901×10^{-8} calorie

1 electron volt = 1.6022×10^{-19} joule
= 1.6022×10^{-12} erg
= 96.487 kJ/mol†

1 litre-atmosphere = 24.217 calories
= 101.32 joules
= 1.0132×10^9 ergs

1 British thermal unit = 1055.06 joules
= 1.05506×10^{10} ergs
= 252.2 calories

Common Units of Length

1 inch = 2.54 centimetres (exactly)

1 mile = 5280 feet = 1.609 kilometres

1 yard = 36 inches = 0.9144 metre

1 metre = 100 centimetres
= 39.37 inches
= 3.281 feet
= 1.094 yards

1 kilometre = 1000 metres
= 1094 yards
= 0.6215 mile

1 Angstrom = 1.0×10^{-8} centimetre
= 0.10 nanometre
= 1.0×10^{-10} metre
= 3.937×10^{-9} inch

Common Units of Force* and Pressure

1 atmosphere= 760 millimetres of mercury
= 1.013×10^5 pascals
= 14.70 pounds per square inch

1 bar = 10^5 pascals

1 torr = 1 millimetre of mercury

1 pascal = 1 kg/ms^2 = 1 N/m^2

Temperature

SI Base Unit: Kelvin (K)

K = -273.15°C

K = °C + 273.15

°F = 1.8(°C) + 32

$$°C = \frac{°F - 32}{1.8}$$

* *Force: 1 newton (N) = 1 kg m/s^2, i.e.,the force that, when applied for 1 second, gives a 1-kilogram mass a velocity of 1 metre per second.*

** *The amount of heat required to raise the temperature of one gram of water from 14.5^{0}C to 15.5^{0}C.*

† *Note that the other units are per particle and must be multiplied by 6.022×10^{23} to be strictly comparable.*

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APPENDIX III

STANDARD POTENTIALS AT 298 K IN ELECTROCHEMICAL

Reduction half-reaction	$E^{\ominus}$/V	Reduction half-reaction	$E^{\ominus}$/V
$H_4XeO_6 + 2H^+ + 2e^- \longrightarrow XeO_3 + 3H_2O$	+3.0	$Pu^{4+} + e^- \longrightarrow Pu^{3+}$	+0.97
$F_2 + 2e^- \longrightarrow 2F-$	+2.87	$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	+0.96
$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O$	+2.07	$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$	+0.92
$S_2O_8^{2-} + 2e^- \longrightarrow 2SO_4^{2-}$	+2.05	$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-$	+0.89
$Ag^+ + e^- \longrightarrow Ag^+$	+1.98	$Hg^{2+} + 2e^- \longrightarrow Hg$	+0.86
$Co^{3+} + e^- \longrightarrow Co^{2+}$	+1.81	$NO_3^- + 2H^+ + e^- \longrightarrow NO_2 + H_2O$	+0.80
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	+1.78	$Ag^+ + e^- \longrightarrow Ag$	+0.80
$Au^+ + e^- \longrightarrow Au$	+1.69	$Hg_2^{2+} + 2e^- \longrightarrow 2Hg$	+0.79
$Pb^{4+} + 2e^- \longrightarrow Pb^{2+}$	+1.67	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.77
$2HClO + 2H^+ + 2e^- \longrightarrow Cl_2 + 2H_2O$	+1.63	$BrO^- + H_2O + 2e^- \longrightarrow Br^- + 2OH^-$	+0.76
$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	+1.61	$Hg_2SO_4 + 2e^- \longrightarrow 2Hg + SO_4^{2-}$	+0.62
$2HBrO + 2H^+ + 2e^- \longrightarrow Br_2 + 2H_2O$	+1.60	$MnO_4^{2-} + 2H_2O + 2e^- \longrightarrow MnO_2 + 4OH^-$	+0.60
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.51	$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	+0.56
$Mn^{3+} + e^- \longrightarrow Mn^{2+}$	+1.51	$I_2 + 2e^- \longrightarrow 2I^-$	+0.54
$Au^{3+} + 3e^- \longrightarrow Au$	+1.40	$I_3^- + 2e^- \longrightarrow 3I^-$	+0.53
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.36	$Cu^+ + e^- \longrightarrow Cu$	+0.52
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+1.33	$NiOOH + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^-$	+0.49
$O_3 + H_2O + 2e^- \longrightarrow O_2 + 2OH^-$	+1.24	$Ag_2CrO_4 + 2e^- \longrightarrow 2Ag + CrO_4^{2-}$	+0.45
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.23	$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$	+0.40
$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + 2H_2O$	+1.23	$ClO_4^- + H_2O + 2e^- \longrightarrow ClO_3^- + 2OH^-$	+0.36
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	+1.23	$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}$	+0.36
$Pt^{2+} + 2e^- \longrightarrow Pt$	+1.20	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$Br_2 + 2e^- \longrightarrow 2Br^-$	+1.09	$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$	+0.27

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$AgCl + e^- \longrightarrow Ag + Cl^-$	+0.27	$S + 2e^- \longrightarrow S^{2-}$	–0.48
$Bi^{3+} + 3e^- \longrightarrow Bi$	+0.20	$In^{3+} + e^- \longrightarrow In^{2+}$	–0.49
$SO_4^{2-} + 4H^+ + 2e^- \longrightarrow H_2SO_3 + H_2O$	+0.17	$U^{4+} + e^- \longrightarrow U^{3+}$	–0.61
$Cu^{2+} + e^- \longrightarrow Cu^+$	+0.16	$Cr^{3+} + 3e^- \longrightarrow Cr$	–0.74
$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+0.15	$Zn^{2+} + 2e^- \longrightarrow Zn$	–0.76
$AgBr + e^- \longrightarrow Ag + Br^-$	+0.07	$Cd(OH)_2 + 2e^- \longrightarrow Cd + 2OH^-$	–0.81
$Ti^{4+} + e^- \longrightarrow Ti^{3+}$	0.00	$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	–0.83
$2H^+ + 2e– \longrightarrow H_2$	(by definition) 0.0	$Cr^{2+} + 2e^- \longrightarrow Cr$	–0.91
$Fe^{3+} + 3e^- \longrightarrow Fe$	–0.04	$Mn^{2+} + 2e^- \longrightarrow Mn$	–1.18
$O_2 + H_2O + 2e^- \longrightarrow HO_2^- + OH^-$	–0.08	$V^{2+} + 2e^- \longrightarrow V$	–1.19
$Pb^{2+} + 2e^- \longrightarrow Pb$	–0.13	$Ti^{2+} + 2e^- \longrightarrow Ti$	–1.63
$In^+ + e^- \longrightarrow In$	–0.14	$Al^{3+} + 3e^- \longrightarrow Al$	–1.66
$Sn^{2+} + 2e^- \longrightarrow Sn$	–0.14	$U^{3+} + 3e^- \longrightarrow U$	–1.79
$AgI + e^- \longrightarrow Ag + I^-$	–0.15	$Sc^{3+} + 3e^- \longrightarrow Sc$	–2.09
$Ni^{2+} + 2e^- \longrightarrow Ni$	–0.23	$Mg^{2+} + 2e^- \longrightarrow Mg$	–2.36
$V^{3+} + e^- \longrightarrow V^{2+}$	–0.26	$Ce^{3+} + 3e^- \longrightarrow Ce$	–2.48
$Co^{2+} + 2e^- \longrightarrow Co$	–0.28	$La^{3+} + 3e^- \longrightarrow La$	–2.52
$In^{3+} + 3e^- \longrightarrow In$	–0.34	$Na^+ + e^- \longrightarrow Na$	–2.71
$Tl^+ + e^- \longrightarrow Tl$	–0.34	$Ca^{2+} + 2e^- \longrightarrow Ca$	–2.87
$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$	–0.36	$Sr^{2+} + 2e^- \longrightarrow Sr$	–2.89
$Ti^{3+} + e^- \longrightarrow Ti^{2+}$	–0.37	$Ba^{2+} + 2e^- \longrightarrow Ba$	–2.91
$Cd^{2+} + 2e^- \longrightarrow Cd$	–0.40	$Ra^{2+} + 2e^- \longrightarrow Ra$	–2.92
$In^{2+} + e^- \longrightarrow In^+$	–0.40	$Cs^+ + e^- \longrightarrow Cs$	–2.92
$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	–0.41	$Rb^+ + e^- \longrightarrow Rb$	–2.93
$Fe^{2+} + 2e^- \longrightarrow Fe$	–0.44	$K^+ + e^- \longrightarrow K$	–2.93
$In^{3+} + 2e^- \longrightarrow In^+$	–0.44	$Li^+ + e^- \longrightarrow Li$	–3.05

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APPENDIX IV

LOGARITHMS

Sometimes, a numerical expression may involve multiplication, division or rational powers of large numbers. For such calculations, logarithms are very useful. They help us in making difficult calculations easy. In Chemistry, logarithm values are required in solving problems of chemical kinetics, thermodynamics, electrochemistry, etc. We shall first introduce this concept, and discuss the laws, which will have to be followed in working with logarithms, and then apply this technique to a number of problems to show how it makes difficult calculations simple.

We know that

$2^3 = 8$, $3^2 = 9$, $5^3 = 125$, $7^0 = 1$

In general, for a positive real number a, and a rational number m, let $a^m = b$,

where b is a real number. In other words

the m^{th} power of base a is b.

Another way of stating the same fact is

logarithm of b to base a is m.

If for a positive real number a, $a \neq 1$

$a^m = b$,

we say that m is the logarithm of b to the base a.

We write this as $\log_a^b = m$,

"log" being the abbreviation of the word "logarithm".

Thus, we have

$\log_2 8 = 3$, Since $2^3 = 8$

$\log_3 9 = 2$, Since $3^2 = 9$

$\log_5^{125} = 3$, Since $5^3 = 125$

$\log_7 1 = 0$, Since $7^0 = 1$

Laws of Logarithms

In the following discussion, we shall take logarithms to any base a, ($a > 0$ and $a \neq 1$)

First Law: $\log_a (mn) = \log_a m + \log_a n$

Proof: Suppose that $\log_a m = x$ and $\log_a n = y$

Then $a^x = m$, $a^y = n$

Hence $mn = a^x . a^y = a^{x+y}$

It now follows from the definition of logarithms that

$\log_a (mn) = x + y = \log_a m - \log_a n$

Second Law: $\log_a \left(\frac{m}{n}\right) = \log_a m - \log_a n$

Proof: Let $\log_a m = x$, $\log_a n = y$

Then $a^x = m$, $a^y = n$

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Hence $\frac{m}{n} = \frac{a^x}{a^y} = a^{x-y}$

Therefore

$$\log_a\left(\frac{m}{n}\right) = x - y = \log_a m - \log_a n$$

Third Law :

$\log_a(m^n) = n \log_a m$

Proof : As before, if $\log_a m = x$, then $a^x = m$

Then $m^n = \left(a^x\right)^n = a^{nx}$

giving $\log_a(m^n) = nx = n \log_a m$

Thus according to First Law: "the log of the product of two numbers is equal to the sum of their logs. Similarly, the Second Law says: the log of the ratio of two numbers is the difference of their logs. Thus, the use of these laws converts a problem of multiplication / division into a problem of addition/subtraction, which are far easier to perform than multiplication/division. That is why logarithms are so useful in all numerical computations.

Logarithms to Base 10

Because number 10 is the base of writing numbers, it is very convenient to use logarithms to the base 10. Some examples are:

$\log_{10} 10 = 1$, since $10^1 = 10$

$\log_{10} 100 = 2$, since $10^2 = 100$

$\log_{10} 10000 = 4$, since $10^4 = 10000$

$\log_{10} 0.01 = -2$, since $10^{-2} = 0.01$

$\log_{10} 0.001 = -3$, since $10^{-3} = 0.001$

and $\log_{10} 1 = 0$ since $10^0 = 1$

The above results indicate that if n is an integral power of 10, i.e., 1 followed by several zeros or 1 preceded by several zeros immediately to the right of the decimal point, then log n can be easily found.

If n is not an integral power of 10, then it is not easy to calculate log n. But mathematicians have made tables from which we can read off approximate value of the logarithm of any positive number between 1 and 10. And these are sufficient for us to calculate the logarithm of any number expressed in decimal form. For this purpose, we always express the given decimal as the product of an integral power of 10 and a number between 1 and 10.

Standard Form of Decimal

We can express any number in decimal form, as the product of (i) an integral power of 10, and (ii) a number between 1 and 10. Here are some examples:

(i) 25.2 lies between 10 and 100

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$$25.2 = \frac{25.2}{10} \times 10 = 2.52 \times 10^{1}$$

(ii) 1038.4 lies between 1000 and 10000.

$$\therefore 1038.4 = \frac{1038.4}{1000} \times 10^{3} = 1.0384 \times 10^{3}$$

(iii) 0.005 lies between 0.001 and 0.01

$$\therefore 0.005 = (0.005 \times 1000) \times 10^{-3} = 5.0 \times 10^{-3}$$

(iv) 0.00025 lies between 0.0001 and 0.001

$$\therefore 0.00025 = (0.00025 \times 10000) \times 10^{-4} = 2.5 \times 10^{-4}$$

In each case, we divide or multiply the decimal by a power of 10, to bring one non-zero digit to the left of the decimal point, and do the reverse operation by the same power of 10, indicated separately.

Thus, any positive decimal can be written in the form

$n = m \times 10^{p}$

where p is an integer (positive, zero or negative) and $1 \leq m < 10$. This is called the "standard form of n."

Working Rule

1. Move the decimal point to the left, or to the right, as may be necessary, to bring one non-zero digit to the left of decimal point.
2. (i) If you move p places to the left, multiply by 10^{p}.
   (ii) If you move p places to the right, multiply by 10^{-p}.
   (iii) If you do not move the decimal point at all, multiply by 10^{0}.
   (iv) Write the new decimal obtained by the power of 10 (of step 2) to obtain the standard form of the given decimal.

Characteristic and Mantissa

Consider the standard form of n

$n = m \times 10^{p}$, where $1 \leq m < 10$

Taking logarithms to the base 10 and using the laws of logarithms

$\log n = \log m + \log 10^{p}$

$= \log m + p \log 10$

$= p + \log m$

Here p is an integer and as $1 \leq m < 10$, so $0 \leq \log m < 1$, i.e., m lies between 0 and 1. When log n has been expressed as p + log m, where p is an integer and 0 log m < 1, we say that p is the "characteristic" of log n and that log m is the "mantissa of log n. Note that characteristic is always an integer – positive, negative or zero, and mantissa is never negative and is always less than 1. If we can find the characteristics and the mantissa of log n, we have to just add them to get log n.

Thus to find log n, all we have to do is as follows:

1. Put n in the standard form, say

$n = m \times 10^{p}$, $1 \leq m < 10$

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2. Read off the characteristic p of log n from this expression (exponent of 10).

3. Look up log m from tables, which is being explained below.

4. Write log n = p + log m

If the characteristic p of a number n is say, 2 and the mantissa is .4133, then we have log n = 2+ .4133 which we can write as 2.4133. If, however, the characteristic p of a number m is say –2 and the mantissa is .4123, then we have log m = –2 + .4123. We cannot write this as –2.4123. (Why?) In order to avoid this confusion we write $\bar{2}$ for –2 and thus we write log m = $\bar{2}.4123$.

Now let us explain how to use the table of logarithms to find mantissas. A table is appended at the end of this Appendix.

Observe that in the table, every row starts with a two digit number, 10, 11, 12,... 97, 98, 99. Every column is headed by a one-digit number, 0, 1, 2, ...9. On the right, we have the section called "Mean differences" which has 9 columns headed by 1, 2...9.

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
61	7853	7860	7868	7875	7882	7889	7896	7803	7810	7817	1	1	2	3	4	4	5	6	6
62	7924	7931	7935	7945	7954	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	6	6
..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..

Now suppose we wish to find log (6.234). Then look into the row starting with 62. In this row, look at the number in the column headed by 3. The number is 7945. This means that

log (6.230) = 0.7945*

But we want log (6.234). So our answer will be a little more than 0.7945. How much more? We look this up in the section on Mean differences. Since our fourth digit is 4, look under the column headed by 4 in the Mean difference section (in the row 62). We see the number 3 there. So add 3 to 7945. We get 7948. So we finally have

log (6.234) = 0.7948.

Take another example. To find log (8.127), we look in the row 81 under column 2, and we find 9096. We continue in the same row and see that the mean difference under 7 is 4. Adding this to 9096, and we get 9100. So, log (8.127) = 0.9100.

Finding *N* when log *N* is given

We have so far discussed the procedure for finding log n when a positive number n given. We now turn to its converse i.e., to find n when log n is given and give a method for this purpose. If log n = t, we sometimes say n = antilog t. Therefore our task is given t, find its antilog. For this, we use the ready-made antilog tables.

Suppose log n = 2.5372.

To find n, first take just the mantissa of log n. In this case it is .5372. (Make sure it is positive.) Now take up antilog of this number in the antilog table which is to be used exactly like the log table. In the antilog table, the entry under column 7 in the row .53 is 3443 and the mean difference for the last digit 2 in that row is 2, so the table gives 3445. Hence,

antilog (.5372) = 3.445

Now since log n = 2.5372, the characteristic of log n is 2. So the standard form of n is given by

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$n = 3.445 \times 10^2$

or n = 344.5

Illustration 1

If log x = 1.0712, find x.

Solution: We find that the number corresponding to 0712 is 1179. Since characteristic of log *x* is 1, we have

$x = 1.179 \times 10^1$

$= 11.79$

Illustration 2

If log x = $\bar{2}.1352$, find x.

Solution: From antilog tables, we find that the number corresponding to 1352 is 1366. Since the characteristic is $\bar{2}$ i.e., –2, so

$x = 1.366 \times 10^{-2} = 0.01366$

Use of Logarithms in Numerical Calculations

Illustration 1

Find 6.3 × 1.29

Solution: Let x = 6.3 × 1.29

Then log x = log (6.3 × 1.29) = log 6.3 + log 1.29

Now,

log 6.3 = 0.7993

log 1.29 = 0.1106

∴ log x = 0.9099,

Taking antilog

x = 8.127

Illustration 2

Find $\frac{(1.23)^{1.5}}{11.2 \times 23.5}$

Solution: Let $x = \frac{(1.23)^{\frac{3}{2}}}{11.2 \times 23.5}$

Then $\log x = \log \frac{(1.23)^{\frac{3}{2}}}{11.2 \times 23.5}$

$= \frac{3}{2} \log 1.23 - \log (11.2 \times 23.5)$

$= \frac{3}{2} \log 1.23 - \log 11.2 - 23.5$

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Now,

$\log 1.23 = 0.0899$

$\frac{3}{2} \log 1.23 = 0.13485$

$\log 11.2 = 1.0492$

$\log 23.5 = 1.3711$

$\log x = 0.13485 - 1.0492 - 1.3711$

$= \bar{3}.71455$

$\therefore x = 0.005183$

Illustration 3

Find $\sqrt{\frac{(71.24)^5 \times \sqrt{56}}{(2.3)^7 \times \sqrt{21}}}$

Solution: Let $x = \sqrt{\frac{(71.24)^5 \times \sqrt{56}}{(2.3)^7 \times \sqrt{21}}}$

Then $\log x = \frac{1}{2} \log \left[\frac{(71.24)^5 \times \sqrt{56}}{(2.3)^7 \times \sqrt{21}}\right]$

$= \frac{1}{2} [\log (71.24)^5 + \log \sqrt{56} - \log (2.3)^7 - \log \sqrt{21}]$

$= \frac{5}{2} \log 71.24 + \frac{1}{4} \log 56 - \frac{7}{2} \log 2.3 - \frac{1}{4} \log 21$

Now, using log tables

$\log 71.24 = 1.8527$

$\log 56 = 1.7482$

$\log 2.3 = 0.3617$

$\log 21 = 1.3222$

$\therefore \log x = \frac{5}{2} \log (1.8527) + \frac{1}{4} (1.7482) - \frac{7}{2} (0.3617) - \frac{1}{4} (1.3222)$

$= 3.4723$

$\therefore x = 2967$

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LOGARITHMS

Table 1

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	5 4	9 8	13 12	17 16	21 20	26 24	30 28	34 32	38 36
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4 4	8 7	12 11	16 15	20 18	23 22	27 26	31 29	35 33
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3 3	7 7	11 10	14 14	18 17	21 20	25 24	28 27	32 31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3 3	6 7	10 10	13 13	16 16	19 19	23 22	26 25	29 29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3 3	6 6	9 9	12 12	15 14	19 17	22 20	25 23	28 26
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3 3	6 6	9 8	11 11	14 14	17 17	20 19	23 22	26 25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3 3	6 5	8 8	11 10	14 13	16 16	19 18	22 21	24 23
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	3 3	5 5	8 8	10 10	13 12	15 15	18 17	20 20	23 22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2 2	5 4	7 7	9 9	12 11	14 14	17 16	19 18	21 21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2 2	4 4	7 6	9 8	11 11	13 13	16 15	18 17	20 19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6471	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

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Table 1 continued

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7768	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9997	9996	0	1	1	2	2	3	3	3	4

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Table 2

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	3	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	3	4	5	6	6

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Table 2 continued

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	42S6	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	1314	
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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